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PHYSICS.—*The elasticity of rubber.*[1]

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INTRODUCTION

The properties of rubber have been regarded in former times as sufficiently novel to call for research activities on the part of a number of scientists better known for their work in other fields. Joseph Priestley, discoverer of oxygen, gave it its name (*36*). Electrician Michael Faraday first measured its chemical composition (*15*). The first to treat the thermodynamics of elastic deformation and to predict temperature and energy changes on the stretching of rubber was none other than Lord Kelvin (*25*), while the first careful experimental investigator of the thermoelastic properties of rubber (*24*) was J. P. Joule, better known for the mechanical equivalent of heat. Boltzmann (*13*) and Kohlrausch (*26*) also each devoted considerable attention to the time-dependent elastic effects in rubber, while W. C. Röntgen (*41*) investigated Poisson's ratio in rubber 20 years before he discovered X-rays.

In the present century the diversity of facts and theories to be considered in natural philosophy has forced such compartmentalization in science that I suspect that few members of the Philosophical Society have ventured very far in considering the nature and origins of the elasticity of rubber. In any case, I should like to outline our present state of knowledge, gained almost entirely in the past 20 years. Reference should be made to several books (*1–6*) for details which can not be included in the present paper.

[1] Address of the Retiring President, Philosophical Society of Washington, January 13, 1956.

Rubbers, natural and synthetic, are unique in their high extensibility and forcible quick retraction. These two properties, in suitable quantitative terms serve as the modern definition of a rubber—independent of any mention of chemical structure.

In Fig. 1 the upper curve represents a typical stress-strain relation obtained with natural rubber (*51*). The lower curve represents values of the stress-temperature intercept at 0° K, which will be discussed later. The upper curve is far from the linearity expressed by Hooke's Law. We note three regions—the first of decreasing slope, the second of almost constant slope, and the third of very rapidly increasing slope. Natural rubber can become semicrystalline on stretching. Measurements of crystallinity by a variety of methods show no evidence of crystals in the first region; in the second region crystallization increases with time; and in the third region the degree of crystallinity may be as high as 30–40 percent and varies little with time.

Fig. 2 shows the same data (*51*) as Fig. 1 with the vertical ordinate or stress scale expanded tenfold. This shows the first two regions and a portion of the third.

Our present conception (*30*) of crystalline regions in a rubber is that the long chain molecules are parallel and alined in those regions and randomly oriented in the amorphous regions. Rubberlike elasticity is possible only in the amorphous regions. The upturn in the stress-strain curve represents the stiffening effect of the crystalline regions in an amorphous matrix. To avoid the complexities associated with a two-

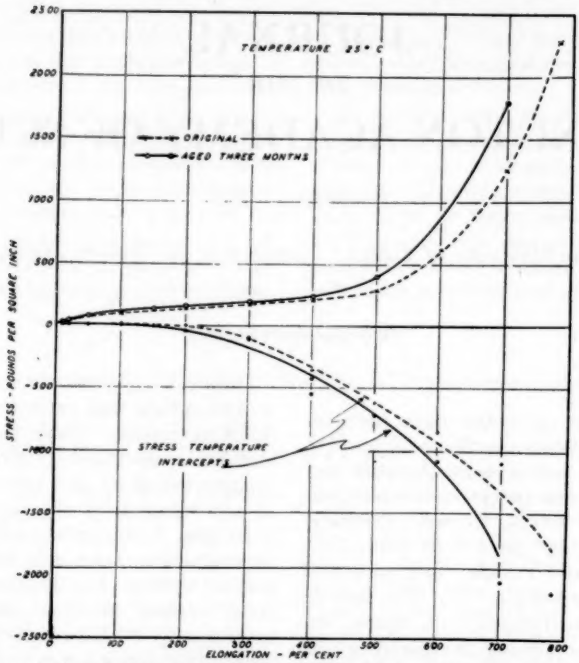

FIG. 1.—Stress-strain relation and stress-temperature intercepts at constant elongation. Natural rubber. Data in Reference *51*.

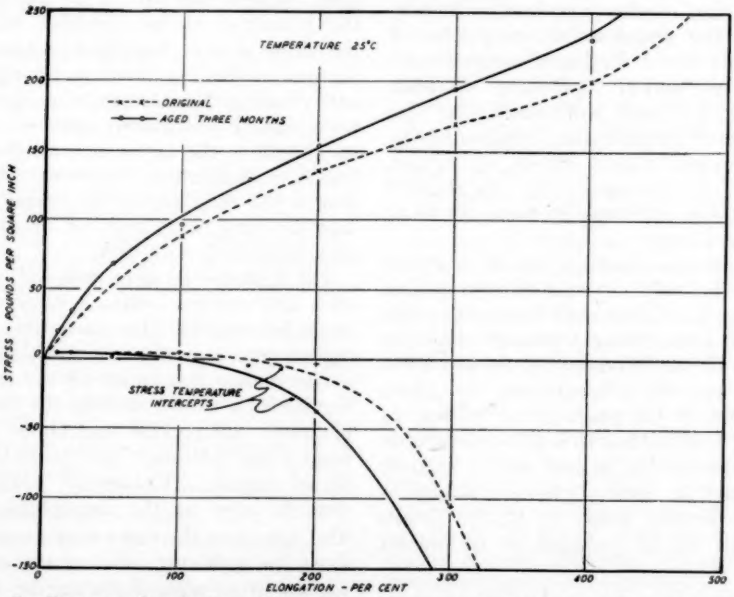

FIG. 2.—Stress-strain relation and stress-temperature intercepts at constant elongation. Ordinate range one-tenth that of Fig. 1. Natural rubber. Data in Reference *51*

phase system we shall concern ourselves hereafter only with effects obtained in the absence of crystallinity and consequently shall consider only the first region of the stress-strain curve.

VISCOELASTIC BEHAVIOR

The relation between stress and strain in rubber is quite time-dependent. The curves already shown were obtained after the stress had been applied for several hours. Fig. 3 shows the stress-strain relations when the specimen is stretched at a constant speed of about 200 percent per minute and then allowed to retract at the same rate. A second extension curve, begun 3 minutes after completion of the first, falls considerably below the first curve, but the second retraction curve is almost identical with the first. The specimen in this case was GR-S—a noncrystallizing copolymer of butadiene and styrene. If the length is held fixed (at 100 percent elongation, for example), the stress is found to decrease with time—rapidly at first and then more and more slowly. If the load is held fixed the length increases rapidly at first and then more and more slowly. The first condition is called stress relaxation; the second is called creep. If the length is held fixed at some point on the retraction curve, one finds an increase of stress with time, or correspondingly a decrease of length with time if the load is held fixed after partial retraction. The curve shown by the dashed line is that obtained after several hours of stress relaxation at each elongation. It is intermediate between the first extension and the retraction curves and is comparable with the curves shown in Figs. 1 and 2 for natural rubber. There is relatively little "set"—namely extension remaining after release of load. Almost all this set disappears in time, as will be seen later, and the discussion will be restricted to rubbers which are sufficiently well-vulcanized to show little significant flow or permanent deformation.

The area under the extension curve represents the work done in deforming the rubber and the area under the retraction curve represents the external work done by the rubber in retracting. The difference

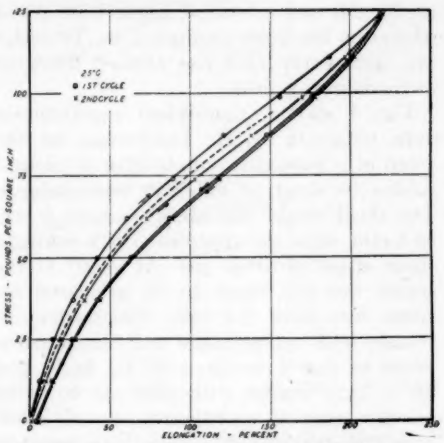

FIG. 3.—Stress-strain relation for extension and retraction at the rate of about 200 percent per minute. There was an interval of about 3 minutes between the two cycles. The dashed line shows stress value after about 2 hours of relaxation at fixed elongation. GR-S synthetic rubber. Data in Reference 42.

between these areas—the area between the curves—represents the irrecoverable energy loss on completing a cycle—in exact analogy with the hysteresis losses in magnetic materials. The loss shown by GR-S synthetic rubber is much larger than is obtained with natural rubber under the same conditions in the absence of crystallization. The loss manifests itself in heat of course and causes GR-S tires to develop higher temperatures than natural rubber tires in operation.

The loss shown by GR-I or Butyl rubber (commonly used in inner tubes) is normally much greater than that shown by GR-S synthetic rubber, particularly if the cycle is traversed rapidly. Dropped from a height of 6 feet a natural rubber ball is deformed in a period of the order of milliseconds and rebounds giving back about 80 percent of its original energy; about 20 percent is lost in hysteresis. A Butyl rubber ball dropped under the same conditions gives back about 8 percent of its original energy; about 92 percent is lost in hysteresis.

Creep, stress relaxation, set, and related effects are examples of viscoelastic phenomena in general. Extensive studies of creep have been made by Leaderman

(*4*, *28*, *29*) and extensive research on stress relaxation has been conducted by Tobolsky (*44*, *45*). Ferry (*16*) has applied dynamic methods in this field.

Fig. 4 shows unpublished experimental data obtained by H. Leaderman on the creep of a pure-gum vulcanizate of natural rubber in shear at different temperatures. The shear strain was observed from 5 sec. to 5 min. after the application of a constant shear stress of 10.67 psi. At −60° C the strain was too small to be measured for times less than 0.5 min. Progressive increases with temperature and time can be noted in Fig. 4 up to −40° C. At 0° and 50° C little change with time can be noted on the scale of coordinates shown. However, the strain at 50° is seen to be less than that at 0° C.

All the data shown in Fig. 4 can be represented in the form of a single sigmoid curve by two successive operations on the coordinates, as follows: (1) plotting as ordinate a quantity equal to the shear strain multiplied by a factor of T/298 where T is the temperature of observation in °K and 298° K (=25° C) is a reference temperature and (2) displacing the curves along the log-time axis until the new ordinate values coincide. The first operation is based on the conclusions of the statistical theory of an equilibrium modulus of rubber elasticity (*5*) to be discussed in more detail in a later section. The second operation is based on a principle of equivalence of time-scale and temperature change which has been extensively investigated (*4*, *16*, *28*, *44*, *45*). The shape of the curves in Fig. 4 is such that, after these operations, coincidence of the overlapping portions of the curves is indeed obtained, and the amount of shift necessary for coincidence of the ordinate values agrees very well with general relations found applicable to all polymers (*16*, *45*).

A single curve is obtained rising in sigmoid fashion from a strain too small to be observed at short times to a shear strain corresponding to a modulus of the order of 10^7 dynes/cm^2 at long times. The curve may be regarded as representing the behavior of the rubber over a very wide range of times at a single reference temperature. The behavior at other temperatures may be obtained by a mere shift of the log-time scale. General confirmation is given to this

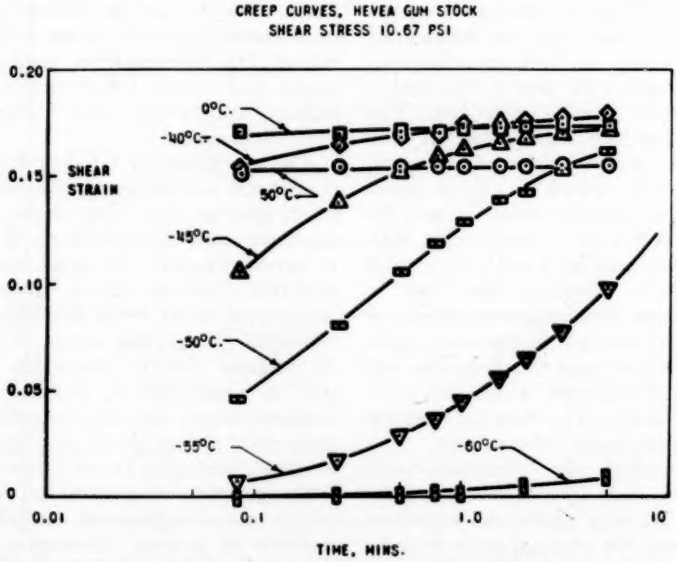

FIG. 4.—Shear creep at various temperatures. Natural rubber. Unpublished data of Leaderman.

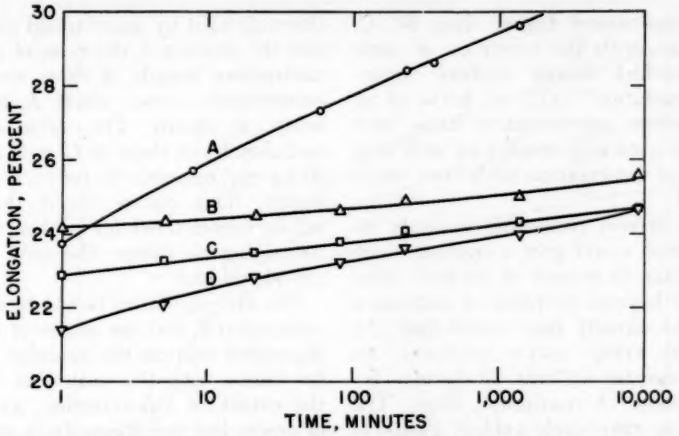

FIG. 5.—Creep at 25°C. Stress about 3 kg/cm² (2kg/cm² for GR-I). A. Neoprene. B. Natural rubber. C. GR-I (Butyl) rubber. D. GR-S. Data in Reference *31*

conception by studies of the dynamic modulus for sinusoidal stresses of varying frequency (*16*). By extending into the megacycle range at 25° C, these studies can give information about the behavior in the range of microseconds, whereas inertial effects prevent direct creep observations on specimens of ordinary size at times shorter than the order of milliseconds.

The sigmoid creep curve for 25° C derived from Fig. 4 indicates that a strip of rubber, in the absence of inertial effects, would first deform perceptibly in a time of the order of hundredths of a microsecond. Other work involving the observation of strains smaller by several orders of magnitude has shown that the effective modulus for shorter times is of the order of 10^{11} dynes/cm². Between about 0.01 microsecond and 10 microseconds the creep curve indicates that the deformation would rise to correspond to a modulus of the order of 10^{7} dynes/cm². The most rapid rise occurs for times of the order of a few microseconds. The slope then shows a steady decrease until the time is of the order of one second, at which point its value is about 2 percent per decade. All the data beyond this time could be represented by a line of constant slope of approximately the same value.

Entirely analogous results are obtained from stress-relaxation experiments (*44*, *45*).

Fig. 5 shows experimental observations of Martin, Roth, and Stiehler (*31*) covering four decades of the creep curve at 25° C beginning at one minute. In this case the specimens were subjected to simple extension at a fixed stress. As far as can be seen the relation of elongation to log time is linear over this range in agreement with the representation of the data of Fig. 4 from one second to 5 minutes. Martin, Roth, and Stiehler (*31*) give the creep of a natural rubber compound vulcanized to approximately the same Young's modulus (13.8 kg/cm²) as the vulcanizate used by Leaderman in Fig. 4 as averaging 2 percent per decade, in agreement with the figure noted for Leaderman's data. The decrease of slope of the creep curve, evident over the range from microseconds to about one second, apparently does not continue over the next six decades of log time.

The maximum time shown in Fig. 5 is about one week, and it is not feasible to extend the observations appreciably farther on the logarithmic time scale at 25° C because of the likelihood of irreversible chemical changes due to aging of the rubber. Likewise degradation and flow (*31*, *42*, *51*) and nonrecoverable stress relaxation (*10*, *11*) occur in most elastomers within a few hours if observations are made at temperatures above 50° C. Thus it is not feasible to extend the effective time-scale by observa-

tions at temperatures higher than 50° C. Consequently, with the exception of some specially purified silicone rubbers "cross-linked by radiation" (*14*), we know of no instances where experimenters have been successful in obtaining conditions such that no change of deformation with time could be observed.

A model system possessing a single retardation time would give a sigmoid creep curve reaching 99 percent of its final value 0.66 decade beyond its point of maximum slope. It has already been noted that the experimental creep curve continues its observable rise for at least 12 decades beyond its point of maximum slope. The conclusion is that each rubber listed in Fig. 5 must be represented as a system with a very wide distribution of retardation times, extending up to at least a week.

Recovery curves at 25° C (*31*) demonstrate that recovery is essentially complete and that the synthetic rubber Neoprene, which showed the greatest slope in its creep curve and had the largest temporary set also recovered most rapidly and its recovery in 10,000 minutes was as complete as that of the others.

The recovery curves demonstrate that a once-stretched rubber is still undergoing changes a week after the stress was removed. The importance of previous mechanical history was also brought out by experiments of Martin, Roth, and Stiehler (*31*) yielding creep curves under a stress of 2 kg/cm² measured (1) after no prestressing, (2) after prestressing for 1440 min. at 4 kg/cm² with no time for recovery, and (3) after prestressing for 1440 min. at 4 kg/cm² followed by 5 min. of recovery at zero stress. It was found that the effects of the 5-minute interval of recovery disappear after about an hour but that the effects of the one-day prestressing are still evident after a week.

FORM OF STRESS-STRAIN RELATION

Suppose that the stress is maintained constant and the strain measured after a fixed period of creep—1,000 min. for example. Fig. 6 shows the results which would be obtained with three different rubber vulcanizates. The ordinate is the stress F (force divided by undeformed cross section) and the abscissa L the ratio of stretched to unstretched length. A short section of the compression curve, where L is less than unity, is shown. The value of Young's modulus M, or slope at $L = 1$, is 10, 15, or 20 kg/cm² respectively for each of the three curves. This covers about the range of values encountered for rubber vulcanizates containing no fillers—the only ones to be considered here.

The first significant fact to be noted in this connection is that the course of the curve is dependent only on the modulus. The modulus varies with the nature of the rubber, the extent of vulcanization, and the time of creep, but the stress-strain relation does not depend on what particular combination of these factors leads to a given modulus. This means that the curves given are applicable for example to any period of creep; of course all points must be taken after the same fixed time. It should be pointed out that the stress-strain curves observed when the stress and strain are varied simultaneously (as in normal tensile testing) do not fulfill this condition.

The second significant fact to be noted is the apparent similarity of shape of the curves. This is demonstrated by plotting the ratio of stress to modulus, F/M, against L. The three curves of Fig. 6 all coalesce to a single general function having unit slope at $L = 1$.

An empirical function representing the observed values of F/M satisfactorily over the range of interest has been found to be:

$$F/M = (L^{-1} - L^{-2}) \exp A(L - L^{-1}) \quad (1)$$

where A is a constant (*31*). A plot of this function including the compression region is shown by the full line in Fig. 7. The constant A has been taken as 0.38. The relation predicted by the statistical theory to be discussed later is shown by the dashed line for comparison. Of course no significance is to be attached to the portion of the empirical curve near the origin. The directly observed values of F/M are found to lie on the full line for values of L between 0.5 and about 3. The data of Martin, Roth, and Stiehler (*31*) offer the best experimental verification

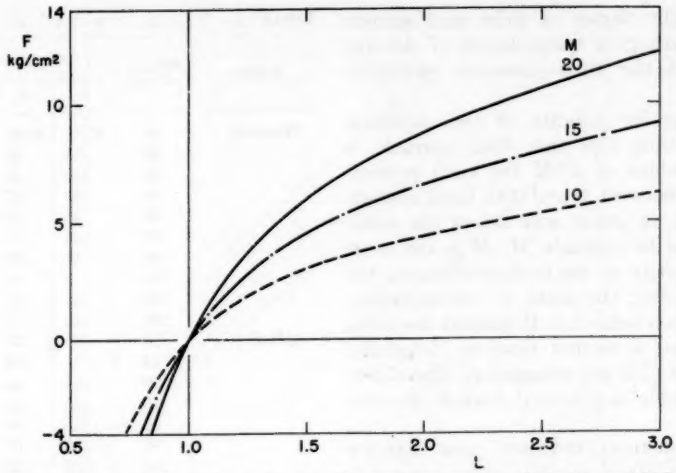

FIG. 6.—Stress-strain relations for rubbers with modulus values of 10, 15, and 20 kg/cm².

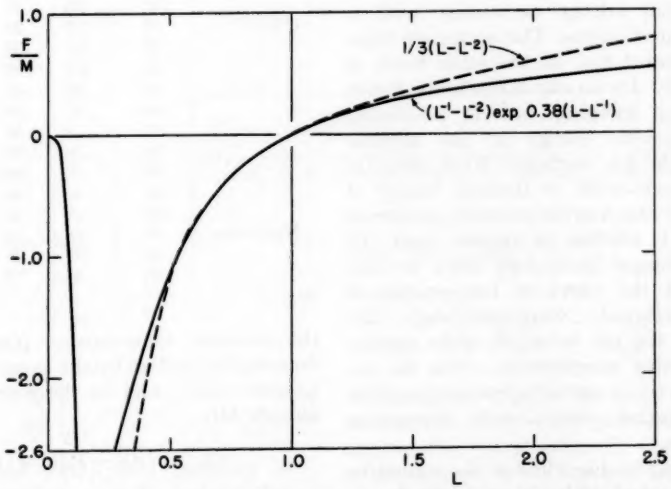

FIG. 7.—Empirical function for relation between stress-modulus ratio F/M and extension ratio L. Dashed line shows function predicted by statistical theory.

of this statement in the region of extension, while the data of Treloar (*47*) offer the most extensive verification in the compression region between $L = 0.5$ and $L = 1$. The observations are better represented by the dashed curve of the statistical theory only for values of L less than 0.5. The success of the single empirical function in representing both compression and extension is a very significant accomplishment.

A more logical and more sensitive method of testing the validity of the empirical F/M function is shown in Fig. 8. The form of the function is such that a plot of the quantities shown as ordinates should yield a straight line with a slope corresponding to the constant A (taken as 0.38 in Fig. 7) and an intercept corresponding to the modulus M. The data (*31*) shown here are for GR-I (Butyl) rubber specimens. Table 1 shows

values of the slopes of these and similar lines for pure-gum vulcanizates of natural rubber and the three common synthetic rubbers.

Accepting the validity of the empirical F/M function one can then compile a table of values of F/M for each percent elongation between 0 and 200; from a single observation of stress and strain the table can be used to evaluate M. M is the most logical quantity to use in characterizing the kind of rubber, the state of vulcanization, and the creep behavior. If desired the table can be used a second time to determine the value of F at any elongation. The utility of such a table in practical work is obvious.

TABLE 1.—VALUES FOR "A" IN EQUATION 1

Rubber	Minutes of cure	Time of creep in minutes			
		1	10	100	1000
Natural	20	0.35	0.36	0.36	0.37
	22	.35	.36	.36	.37
	25	.35	.36	.36	.37
	30	.36	.37	.36	.37
	40	.36	.37	.37	.37
	60	.36	.37	.37	.37
	80	.36	.36	.37	.37
	100	.36	.37	.38	.38
	120	.36	.37	.38	.38
	240	.36	.37	.37	.38
GR-S	20	.33	.33	.34	.36
	25	.34	.34	.35	.37
	30	.34	.34	.35	.38
	40	.35	.35	.36	.38
	60	.35	.36	.36	.38
	80	.35	.37	.37	.38
	100	.36	.37	.37	.38
	120	.36	.37	.37	.38
	160	.36	.37	.37	.38
	240	.36	.37	.37	.38
GR-I	20	.32	.33	.34	.36
	22	.33	.34	.36	.37
	25	.34	.36	.37	.38
	30	.36	.37	.38	.39
	40	.37	.38	.38	.39
	60	.38	.38	.39	.40
	80	.39	.40	.40	.40
	100	.39	.40	.40	.41
	160	.40	.40	.41	.40
	240	.40	.41	.41	.42
Neoprene	20	.38	.38	.38	.39
	40	.38	.38	.39	.40
	90	.38	.39	.39	.40

THERMODYNAMICS: ENTROPY AND ENERGY

The retractive force in a stretched metal can be traced back to interatomic forces and potential energy associated with a displacement of atoms. The expansive force of a compressed gas, on the other hand, is not primarily due to any interatomic forces or potential energies, but is associated with the kinetic energy of the thermal motion of the gas particles. Work done on the gas is converted to thermal energy of the particles and may be partially recovered as the gas is allowed to expand again. In this case changes in entropy must be considered and the effect of temperature is highly significant. Correspondingly the pressure of the gas increases quite rapidly with increasing temperature, while the retractive force in a stretched metal generally decreases rather slowly with increasing temperature.

One can determine whether the retractive force in stretched rubber is primarily due to interatomic forces (as in the metal) or to entropy changes (as in the gas) from an examination of stress-temperature relations (*32*). Thermodynamic considerations can be applied to derive quantitative relations involving "equilibrium" (i.e., time-independent) values of the stress. We shall follow the thermodynamic treatment and symbols of Flory (*3*) in this section.

The change in internal energy dE in a process is the sum of the heat energy added TdS, where dS is the entropy change and T the absolute temperature, plus the work done on the system by the external pressure, namely $-PdV$ and by the retractive force, namely fdL.

$$dE = TdS - PdV + fdL \qquad (2)$$

where f is the force and dL the distance through which the force acts.

The Gibbs free-energy F and the Helmholtz energy function A are defined as follows:

$$F = E + PV - TS = A + PV \quad (3a, b)$$

The change in free energy dF in a process can be obtained by differentiation of Eq. (3a) to give

$$dF = VdP - SdT + fdL \qquad (4)$$

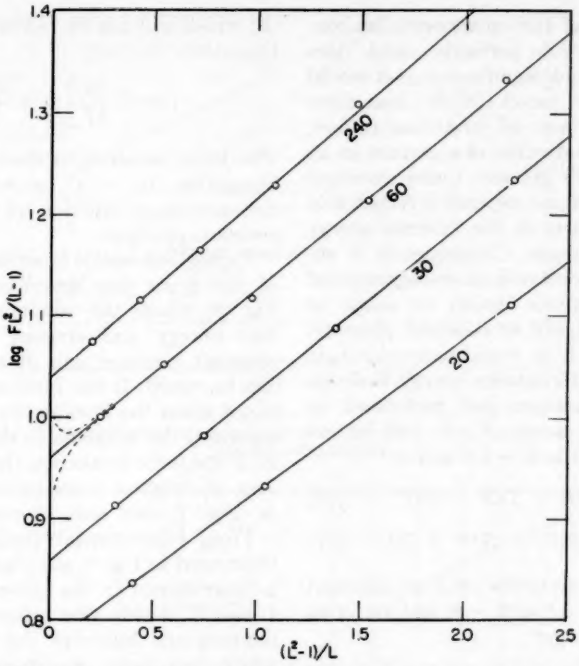

FIG. 8.—Plot for determining validity of empirical function and evaluating the constant A and the modulus M. GR-I (Butyl) rubber vulcanized 20, 30, 60, and 240 minutes. 100 min. creep. Data in Reference *31*.

It can be seen that

$$\left.\frac{\partial F}{\partial L}\right]_{T,P} = f \qquad (5)$$

and

$$\left.\frac{\partial F}{\partial T}\right]_{L,P} = -S \qquad (6)$$

Utilizing the well-known property of a double partial derivative that the order of differentiation is immaterial one finds that

$$\left.\frac{\partial f}{\partial T}\right]_{L,P} = \left.\frac{-\partial S}{\partial L}\right]_{T,P} \qquad (7)$$

The quantity on the right is significant in calculations but not directly observable. The quantity on the left is readily measured.

Solving Equation (2) for the force one finds:

$$f = -T\left.\frac{\partial S}{\partial L}\right]_{T,P} + \left.\frac{\partial E}{\partial L}\right]_{T,P} \qquad (8)$$

since the quantity $P\left.\frac{\partial V}{\partial L}\right]_{T,P}$ is negligible. Finally,

$$f = T\left.\frac{\partial f}{\partial T}\right]_{L,P} + \left.\frac{\partial E}{\partial L}\right]_{T,P} \qquad (9)$$

This means that if the force f measured at constant length and pressure is plotted against the temperature T, then the slope of the tangent to the curve at any point will give $\left.\frac{-\partial S}{\partial L}\right]_{T,P}$ and the intercept (at 0° K) of the tangent will give $\left.\frac{\partial E}{\partial L}\right]_{T,P}$.

Plots of this sort are frequently made (*7*, *8*), and are usually found to be practically linear. The entropy component of the force $-T\left.\frac{\partial S}{\partial L}\right]_{T,P}$ is often found to be considerably larger than the energy component $\left.\frac{\partial E}{\partial L}\right]_{T,P}$ but the latter is by no means negligible in general.

This analysis of the components at constant pressure, while perfectly valid, does not possess as much significance as it would if it had not been found (*20*, *21*) that there is a volume increase on stretching rubber, amounting to hundredths of a percent at an elongation of 100 percent under constant pressure. This volume increase is responsible for significant parts of the internal energy and entropy changes. Consequently if attention is to be centered on configurational aspects, the analysis should be made at constant volume, not at constant pressure.

In this case, it is found convenient to perform on the Helmholtz energy function A the same operations just performed on the Gibbs free energy F. It will be remembered that A is $E - TS$ and so

$$dA = dE - TdS - SdT \qquad (10)$$

$$dA = -PdV - SdT + fdL \qquad (11)$$

The partial derivatives of A at constant volume are again f and $-S$ and on cross differentiation we get

$$\left.\frac{\partial f}{\partial T}\right]_{L,V} = \left.\frac{-\partial S}{\partial L}\right]_{T,V} \qquad (12)$$

$$f = T\left.\frac{\partial f}{\partial T}\right]_{L,V} + \left.\frac{\partial E}{\partial L}\right]_{T,V} \qquad (13)$$

This is identical in form with Equation (9) previously obtained at constant pressure. It calls for maintaining the volume constant by the application of external pressure as the force-temperature relation is investigated. This would be an experimental condition quite difficult to maintain accurately, although consideration has been given to attempting it.

The same result can be obtained under much simpler experimental conditions if one makes use of the following approximation:

$$\left.\frac{-\partial S}{\partial L}\right]_{T,V} = \left.\frac{\partial f}{\partial T}\right]_{\alpha,P} \qquad (14)$$

where α is the ratio of stretched to unstretched length, the lengths being measured at the same temperature. This approximation may be derived by an extended analysis (*3*) which will not be repeated here. Finally then

$$f = T\left.\frac{\partial f}{\partial T}\right]_{\alpha,P} + \left.\frac{\partial E}{\partial L}\right]_{T,V} \qquad (15)$$

The force required to maintain a constant elongation, $(\alpha - 1)$, is relatively easy to measure as a function of temperature at constant pressure.

Typical schematic force-temperature plots of the types just described are shown in Fig. 9, where the resolution of the force into energy and entropy components at constant pressure and at constant volume can be noted. If the force-temperature plot is not linear the lines shown can be taken to represent the tangents to the curve at point D. If the force is taken as that acting on unit area of original cross section the ordinate in Fig. 9 can also represent the stress.

From experimental studies of the type illustrated in Fig. 9 one obtains data similar to that shown in the lower curves of Figs. 1 and 2, which give values of the stress-temperature intercept for natural rubber which has been maintained at constant elongation for several hours (*51*). This period is long enough to insure that the stress is changing only very slowly with time. However, the true "equilibrium" values required in the thermodynamic analysis are not experimentally accessible, since the stress relaxation of natural rubber at 25° C, like the creep, is normally not less than the order of 2 percent per decade of time, as discussed in the section on viscoelastic behavior. Some observers have reduced the rate of stress relaxation at 25° C by a previous relaxation at the maximum elongation followed by a recovery period (*22*) or by a previous swelling of the rubber (*18*, *20*). It is not clear to what extent these procedures may alter the system under investigation.

The intercept of the stress-temperature relation represents, as has just been shown, the internal energy component $\left.\frac{\partial E}{\partial L}\right]_{T,V}$ of the stress. The negative values at high elongations are due to crystallization, which of course is responsible for large changes in internal energy with stretching. Crystalliza-

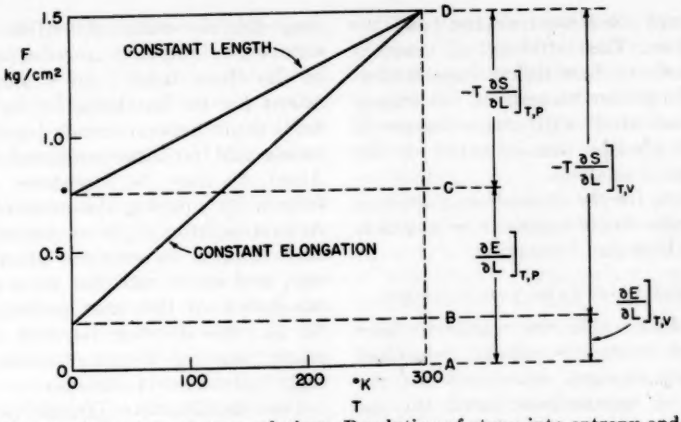

FIG. 9.—Stress-temperature relations. Resolution of stress into entropy and energy components.

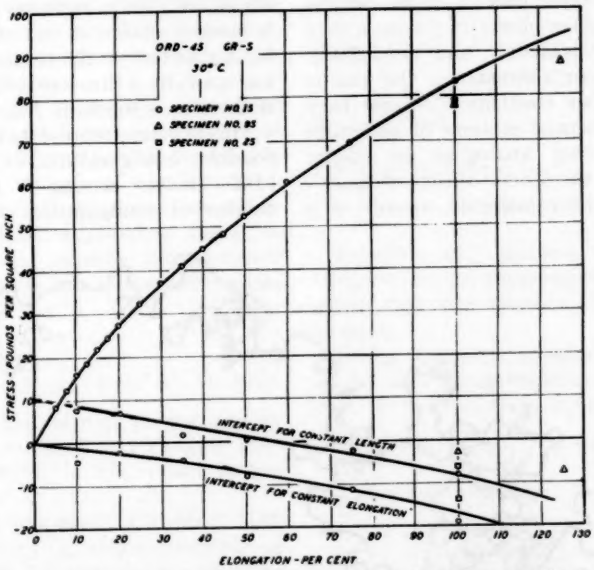

FIG. 10.—Stress-strain relation and stress-temperature intercepts for GR-S. Data in Reference *42*.

tion by favoring the alinement of molecules in the direction of stretching would be expected to decrease the total force and lead to negative values of the intercept. The positive values which are obtained at low elongations have not received an explanation in molecular terms, but are quite small in comparison with the total stress. The total stress is consequently to be regarded as consisting essentially of the entropy component alone in the case of natural rubber in the absence of crystallization.

A similar type of representation of the results (*42*) obtained with GR-S synthetic rubber is given in Fig. 10. The constant-elongation intercept is always negative here, becoming zero at the zero elongation. Thus the observed stress is consistently

less than that component arising from the entropy alone. The intercept at constant length also shown here differs from that at constant elongation because of the energy changes associated with the change of volume, as already demonstrated in the thermodynamic analysis.

Similar data for the evaluation of internal energy changes do not appear to be available for Butyl rubber and Neoprene.

STATISTICAL CALCULATION OF ENTROPY

The conclusion that the retractive force in stretched rubber is chiefly associated with entropy changes stimulated the development of calculations based on the detailed molecular structure of rubber (*5*, *48*). These calculations and related background are commonly called the statistical theory of rubber elasticity (because they are based on statistics and probability considerations) or alternatively the kinetic theory of rubber elasticity (because they relate to the thermal motions of molecular segments and are analogous to similar calculations in the kinetic theory of gases).

A typical rubber molecule consists of a long flexible chain of 10,000 to 100,000 atoms. For simplicity, numbering the atoms in the chain from 1 to n and neglecting atoms not in the chain, let us maintain a fixed angle between bonds joining adjacent atoms and no other preferred orientation. Atom A_3 may lie anywhere on a circle formed by rotating the molecule about A_1 A_2 as axis; atom A_4 is correspondingly on a circle formed by rotation about A_2 A_3 as axis, and so on with the other atoms. The calculation of the most probable value of A_1 A_n, the distance between ends, is of course one of the well-known "random flight" problems of statistics.

For visualization Treloar (*5*) has constructed a model of this sort by bending a wire to make 1,000 equal segments with angles of 109° between each segment. A random choice of one of 6 positions for A_3, A_4, A_5, etc. on the circles just mentioned was made by a throw of a die. A photograph of the wire is shown in Fig. 11.

This of course represents only one of many possible configurations. Since there are 1,000 choices among 6 possibilities the number of configurations is 6^{1000}, which is

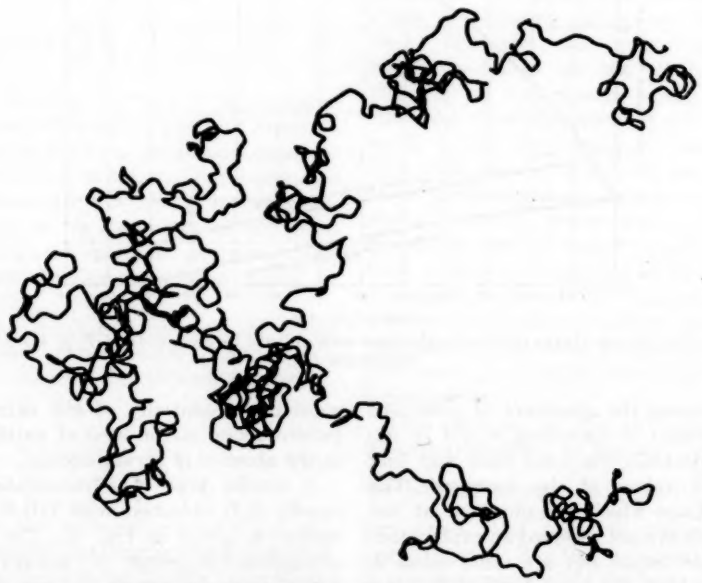

FIG. 11.—1000-link chain with random orientation of links. Described on page 42 of Reference *5*.

10^{778}. The end-to-end distance $A_1 A_n$ shown turned out to be very close to the most probable end-to-end distance calculated from statistics. The actual typical rubber molecule would have a minimum of about 10,000 links rather than the 1,000 shown here.

We shall not trace out any exact derivations here but it is easy to see that one can calculate the probability of a given configuration and of a given ensemble of configurations. From this the entropy of the undeformed rubber can be obtained by the Boltzmann relation that the entropy is the Boltzmann constant k times the logarithm of the probability. A similar calculation can be made for the entropy in the deformed state. The difference in entropies multiplied by the temperature gives the change in the Helmholtz energy function A on stretching, or at least that portion of it which arises from entropy changes.

Three somewhat different approaches have been used for these calculations of change of A on deformation. If the dimensions of a cube, initially of unit length on each side, become λ_1, λ_2, and λ_3 on deformation, the three approaches agree in predicting that the entropy component of the energy function change per unit volume should have the form:

$$\Delta A = -T\Delta S = (G/2)\,(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3) \quad (16)$$

They also agree in predicting proportionality between the constant G and absolute temperature but differ in the other factors determining G.

The approach proposed by Kuhn (*23*, *27*, *46*) considers only a single molecule of molecular weight M_c and assumes that the deformations of the molecule parallel exactly the deformations of the bulk rubber. This approach yields

$$G = \rho RT/M_c \quad (17)$$

where ρ is the density and R the gas constant.

The approach proposed by F. T. Wall (*46*, *50*) considers N chains and yields

$$G = NkT \quad (18)$$

where k is the Boltzmann gas constant.

The approach outlined by Flory and Rehner (*3*, *19*, *49*) considers a network resolved into tetrahedra of average molecular weight M_c between cross-links. The result is the same as that given in Equation (17), where M_c now has the significance just mentioned.

If the specimen is subject to the type of deformation known as pure shear $\lambda_1 = L$, $\lambda_2 = 1/L$ and $\lambda_3 = 1$, where L is the ratio of stretched to unstretched length for one dimension of the unit cube. When the deformation is simple shear (involving effectively a translation and rotation in addition to pure shear) the shear strain γ is $(L - 1/L)$ and the strain energy is the same as for pure shear.

The strain energy per unit volume for simple shear is thus from Equation (16):

$$W = (G/2)(L^2 + 1/L^2 - 2) = (G/2)(L - 1/L)^2 \quad (19)$$

$$W = (G/2)\gamma^2 \quad (20)$$

The shear stress σ is then:

$$\sigma = dW/d\gamma = G\gamma \quad (21)$$

Equation (21) predicts the validity of Hooke's Law for shear stress and strain and states that the constant G is the shear modulus.

If the specimen is subjected to simple extension or compression $\lambda_1 = L$ and $\lambda_2 = \lambda_3 = L^{-\frac{1}{2}}$. Here, from Equation (16),

$$W = (G/2)(L^2 + 2/L - 3) \quad (22)$$

and the stress F is then

$$F = \frac{dW}{dL} = G(L - L^{-2}) \quad (23)$$

One notes that the slope of Equation (23) at the origin is $3G$; consequently Young's Modulus M is three times the shear modulus G,—the relation valid for an incompressible material.

$$F/M = (1/3)(L - L^{-2}) \quad (24)$$

Experimental values of the entropy components of stress can be obtained by subtracting from an observed value of total

stress the component due to energy effects. The methods of determining the latter quantity are given in the preceding section. Figs. 1 and 2 show observed values of total stress (upper curves) and energy component (lower curves) for a pure-gum vulcanizate of natural rubber. Up to elongations (about 150 percent) where crystallization becomes apparent in this rubber the energy component is rather small compared with the total stress; consequently in this instance the total stress arises effectively from the entropy component alone. In Fig. 7 the values of entropy component of the stress-modulus ratio (dashed line) calculated from Equation (24) derived from the statistical theory are compared with the observed values represented by the empirical relation (full line) given by Equation (1). It will be seen that the discrepancy between the observed values and the calculated values is considerable; the calculated values are as much as 50 percent larger than the observed values at $L = 3$. This discrepancy has been noted repeatedly in natural rubber (*5*, *8*, *22*, *31*, *43*, *47*, *49*), but no revised calculation of the entropy component has been developed which will explain the discrepancy. The discrepancy appears also in Butyl rubber (*17*) and in silicone rubber (*14*).

In the case of a pure-gum vulcanizate of GR-S synthetic rubber (*42*) the discrepancy is found to be much less. Here the energy component is much larger, is always negative, and its magnitude increases markedly with elongation, as can be seen in Fig. 10. When this quantity is added to the observed stress to get an experimental value of the entropy component of the stress-modulus ratio, it is found that the value calculated from statistical theory seldom exceeds this experimental value by more than 10 percent. It is difficult to understand how GR-S should come nearer to the ideal rubber in this respect and yet be farther from it in most other respects.

The statistical theory, in addition to the predictions regarding the functional form of the stress-strain relation as just discussed, calls for proportionality between the shear modulus G and absolute temperature, Equations (17) and (18). This proportionality is normally found to be valid (*7*, *32*, *42*, *51*). When precise measurements are made at low elongations, curves which are concave toward the temperature axis are observed (*8*).

Finally the statistical theory in Equations (17) and (18) predicts a definite value of the shear modulus, which can be calculated if one can determine M_c or N. The first attempts (*9*, *17*, *18*) to verify the relationship gave values of the calculated modulus between one-third and one-half of those which are observed. Very recent extensive studies (*34*, *35*) have given calculated values as high as two-thirds of those observed. In the calculation a correction must be made for the effect of initial molecular weight before cross linking. Network entanglements, not considered in the measured cross linkages, are usually considered responsible for the higher observed modulus. On the other hand, in very recent work on silicone rubber cross-linked by radiation Bueche (*14*) calculates a modulus about twice that observed.

STRAIN ENERGY CONSIDERATIONS

We have just seen how a single strain energy function can be used to predict stress-strain relations under two different types of deformation. Indeed if completely known, it can predict these relations for any arbitrary type of deformation whatever. We can say then that the ultimate problem of rubber elasticity is the derivation of the strain energy function from molecular considerations. We have seen the rather limited success of the statistical calculation of the entropy component.

There are certain general considerations regarding the form of the strain energy function which must apply whatever its molecular origin. Work along these lines was initiated by Mooney (*33*) and the ideas were put into much more general and rational form by Rivlin (*37–40*). For example, the strain energy function must be expressible as a linear combination of certain functions of the deformation called strain invariants. The three simplest strain invariants are as follows:

$$I_1 = \lambda_1^2 + \lambda_2^2 + \lambda_3^2 \qquad (25)$$

$$I_2 = \lambda_1^2\lambda_2^2 + \lambda_2^2\lambda_3^2 + \lambda_3^2\lambda_1^2 \quad (26)$$

and

$$I_3 = \lambda_1^2\lambda_2^2\lambda_3^2 \quad (27)$$

Each must fulfill two conditions: first, it must be symmetrical in λ_1, λ_2, and λ_3, because of the isotropy of the rubber before stretching, and second, it must contain only even powers of the λ's, since the stored energy is unaltered by a change of sign of two of the λ's, corresponding to a rotation of the deformed rubber through 180°. It can be seen that each term in I_1 contains a single λ; in I_2 they appear in pairs and in I_3 they appear as the product of all three. Higher strain invariants contain the fourth and higher even powers of the λ's, but will not be further considered here because of their complexity.

If the volume is constant (as it is in rubber to within some hundredths of a percent), I_3, the square of the volume of the deformed unit cube, is equal to unity and I_2 becomes the sum of the reciprocals of the squares of the λ's.

For simple extension the relations have already been mentioned

$$\lambda_1 = L, \qquad \lambda_2 = \lambda_3 = L^{-\frac{1}{2}},$$

and consequently

$$I_1 = L^2 + 2L^{-1} \quad (28)$$

and

$$I_2 = 2L + L^{-2} \quad (29)$$

The stress F for simple extension or compression can be obtained by differentiation of the strain energy function W.

$$F = \frac{dW}{dL} = \frac{\partial W}{\partial I_1}\frac{dI_1}{dL} + \frac{\partial W}{\partial I_2}\frac{dI_2}{dL} \quad (30)$$

I_3 does not appear since it is unity, as already mentioned, and higher invariants are being neglected.

$$F = 2(L - L^{-2})\frac{\partial W}{\partial I_1} + 2L^{-1}(L - L^{-2})\frac{\partial W}{\partial I_2} \quad (31)$$

If one wishes to put Equation (31) into a form suitable for a convenient plot, he has two choices suggested by the following two modifications of the equation:

$$(F/M)/2(L - L^{-2}) = \frac{1}{M}\frac{\partial W}{\partial I_1} + \frac{1}{M}\frac{\partial W}{\partial I_2}L^{-1} \quad (32)$$

$$(F/M)/2(1 - L^{-3}) = \frac{1}{M}\frac{\partial W}{\partial I_1}L + \frac{1}{M}\frac{\partial W}{\partial I_2} \quad (33)$$

If in accordance with the conclusion of Mooney (*33*), the partial derivatives remain constant as L is varied, a plot of

$$(F/M)/2(L - L^{-2}) \text{ against } L^{-1}$$

as suggested by Equation (32) will give a straight line with intercept

$(1/M)(\partial W/\partial I_1)$ and slope $(1/M)(\partial W/\partial I_2)$.

The converse of this statement is not true: if a straight line is obtained from a plot of the type mentioned it is not necessarily true that the intercept C_1/M and slope C_2/M will be the quantities mentioned, since the partial derivatives may each be functions of L. Rivlin and Saunders (*39*) present evidence to indicate that $\partial W/\partial I_1$ is substantially independent of I_1 and I_2, and consequently independent of L. $\partial W/\partial I_2$ is independent of I_1 but decreases with increase of I_2. However the decrease is not more than about ten percent over the range considered here. A plot similar in form to that just mentioned but not containing the factor M has found extensive use (*22*, *39*, *40*, *43*) in the British literature.

If the plot just mentioned is not a straight line the slope and intercept may be evaluated over limited regions of approximate linearity. Fig. 12 shows the empirical F/M function given in Equation (1) with A = 0.38, used in a plot differing only by a constant factor from that suggested by Equation (32). An approach to linearity is seen for the intermediate values of L^{-1}.

Equation (33) suggests a plot of $(F/M)/2(1-L^{-3})$ against L to evaluate as intercept C_2/M and as slope C_1/M. This general type of plot has been noted in only one

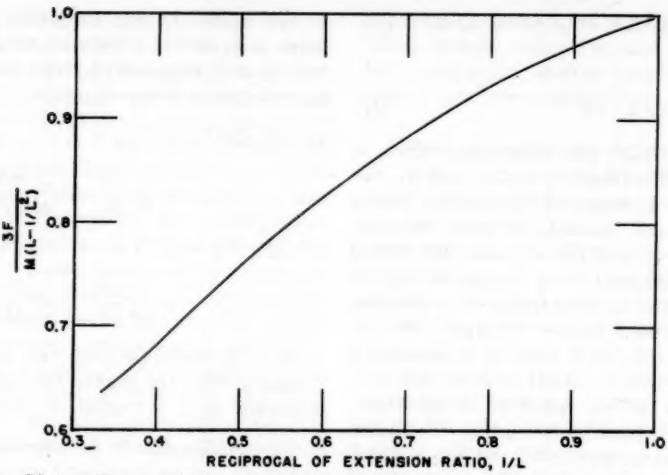

FIG. 12.—Plot of the empirical stress-strain relation of Eq. (1) in the form suggested by Eq. (32). A taken as 0.38.

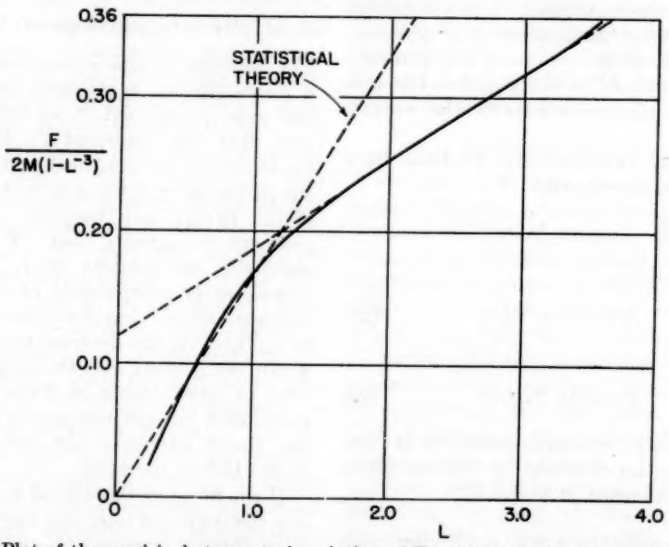

FIG. 13.—Plot of the empirical stress-strain relation of Eq. (1) in the form suggested by Eq. (33). A taken as 0.38.

instance (*12*) (again without the factor M), although this form appears to be much more convenient and is more readily visualized than that suggested by Equation (32). The region of compression also is represented in a more satisfactory fashion.

Fig. 13 demonstrates the same facts as Fig. 12 somewhat more clearly by using the empirical F/M function in the plot suggested by Equation (33). This figure extends into the region of compression. It shows that in this region the statistical theory represents the data adequately. In fact, for values of L below 0.5 and only in this region, it has already been pointed out that the statistical theory represents the data

better than the empirical F/M function. The deviations from the statistical theory are apparent immediately above $L = 1$; there is no region of approximate conformity at low values of extension.

For values of L between 1.5 and 3 a straight line with smaller slope and a positive intercept is noted, corresponding to the approach to linearity noted in Fig. 12. Both slope and intercept are varying in the region from 1.0 to 1.5.

Crystallization effects (*3*, *39*), lack of reversibility (*40*), and the approach to the limiting extension of a network (*39*, *40*, *49*) have been invoked to explain the behavior for values of L greater than 3. There has been a tendency to ascribe the deviations from linearity for L between 1.0 and 1.5 (i.e., for L^{-1} between 0.7 and 1) to errors of observation (*22*) but the deviations are systematic and the line must form a smooth junction with the values in the compression region (L less than 1), as shown in Fig. 13.

The entropy component of the strain energy function predicted by the statistical theory has been given in the preceding section as Equation (16). This is now seen to involve only the first strain invariant I_1 and constants. It is the simplest possible form the strain energy function could assume. The statistical theory offers no explanation of the term involving the second strain invariant I_2 above $L = 1.0$, as shown in Fig. 13. The defect, in the case of natural rubber at least, is in the calculated entropy and not in the internal energy term, as has just been shown by the thermodynamic analysis. The decrease of entropy with L is less at larger values of L than would be calculated from pure probability. In other words, the system retains more disorder in the arrangement of the molecular chains than is expected. This is not too surprising. The quantitative calculation of this additional entropy from molecular considerations is one of the most promising fields for further work in the theory of rubber elasticity.

SUMMARY

Rubbers, natural and synthetic, are unique in being highly extensible and in retracting forcibly and quickly to substantially their original dimensions when released.

It has been found that the stress-strain curves for extension and compression of most of the simplest vulcanizates of natural rubber and the three most important synthetic rubbers are similar in shape. The relationship is expressed by the equation $F/M = (L^{-1} - L^{-2}) \exp A(L - L^{-1})$ where F is the stress, L the ratio of stretched to unstretched length, and M and A are constants. The constant M depends on the nature of the rubber, the extent of vulcanization, and the time of creep. The constant A has a value of about 0.38.

By a study of stress-temperature relations it is found that the most important factor in the retraction of stretched rubber is the tendency of long chain flexible molecules to return to a configuration which is statistically more probable than the one which the stretching has forced them to assume. Calculations of entropy changes arising from stretching can be made from probability considerations, and a strain energy function deduced from the entropy changes. Stresses calculated from the strain energy function agree with those observed in compression but are greater than those observed in extension by almost 50 percent at $L = 3$.

A phenomenological approach shows that the strain energy should be expressible as a function of certain quantities called strain invariants, calculable from the deformations. The simplest behavior is found in the region of compression (L less than 1), where the strain energy is merely the first invariant times a constant calculable from the entropy changes. For values of L between 1.5 and 3 a different constant and an added term involving the second strain invariant are required. The explanation of this behavior in molecular terms is one of the most important current problems of rubber elasticity.

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THE GRASSES OF WASHINGTON

A new publication has just appeared by which the grasses of this area may be identified. This is *Grasses of the Tidewater-Piedmont region of northern Virginia and Maryland* by Mrs. Elizabeth M. Gilman; published in Castanea **22** (1): 1–105, illus. 1957.

Mrs. Gilman, long a student of grasses, has prepared this as a contribution toward the projected new Flora of the Washington-Baltimore Area. It is a manual with keys and descriptions. This region contains 191 established species and varieties, besides a few waifs and adventives. This small manual is a welcome replacement of the grass treatment in Hitchcock and Standley's *Flora of the District of Columbia and vicinity* issued in 1919, long out of print and now out of date. It was prepared with all the resources of the world-famous grass herbarium of the U. S. National Herbarium in the Smithsonian Institution and under the guidance of Mrs. Agnes Chase, its honorary custodian.

Reprints, with weather-repellent covers, may be obtained for $1.00 from Dr. E. H. Walker, Chairman of the Conference on District Flora, c/o Smithsonian Institution, Washington 25, D. C.

CHEMISTRY.—*Chemistry at high pressures and high temperatures.*[1] H. TRACY HALL, Brigham Young University, Provo, Utah. (Communicated by P. H. Abelson.)

It is now possible to do experimental work on a small scale at pressures of 3 million pounds per square inch up to temperatures of 5,000°C. This new pressure-temperature field was opened by the author's design of an apparatus known as the "belt" while at the General Electric Co. in January 1953. It was in this apparatus that the author succeeded in making diamonds late in 1954. Fig. 1 shows this new pressure-temperature region in comparison to the region that was accessible prior to this development.

The significance of the opening of this hitherto unavailable experimental region will now be discussed. The physical and chemical changes that can be produced in a system are qualitatively related to the "intensity factor" (pressure, temperature, volts, etc.) of the energy that is put in to the system. Energy, of course, can be injected in to systems in various forms. One of the most important types of energies has been heat energy. One cubic centimeter kilo atmosphere is equivalent to 12.19° Kelvin.

It is now possible to expect to cause changes in condensed systems by application of pressure alone that are comparable to those formerly brought about by application of temperature alone.

In many respects pressure and temperature are diametric opposites, high pressure being equivalent to low temperature. As temperature is increased, solids transform to liquids, which in turn become gases. Systems then proceed to products of molecular dissociation, and finally, at sufficiently high temperatures, the atomic nucleii will be separated from the electrons by electronic dissociation. On the other hand, increasing high pressures cause gaseous systems to become liquids, which in turn transform to solids. This is followed by collapse of electronic shells and, at pressures of billions of atmospheres, nuclear fusion.

The general effect of high pressure in regard to reaction rates is one of reducing the rate. Therefore, in order to have a chemical reaction take place under high-pressure conditions in a reasonable length of time, it is almost always desirable to operate at high temperature. A detailed consideration of the thermodynamics and reaction rates of systems has been given elsewhere.[2]

The general problem of finding the region in a pressure-temperature field where a reaction will proceed at a measurable or useful rate is one of constructing a free-energy-equals-0 line from the thermodynamics of the system involved, coupled with the problem of determining a minimum-rate line as a function of pressure and temperature. The desired products will be made from the reactants in the region of overlap of these two curves above the free-energy-equals-0 line.

Pressures now available are great enough to influence strongly the external electronic configuration of atoms. Since chemistry depends on the characteristics of the external electrons, the ordinary chemical behavior of atoms can be drastically changed by the application of high pressure. Indeed, it is possible to force outermost electrons into vacant inner shells. This pressure effect on the external electrons is the most fascinating aspect of high-pressure research for the immediate future; for it should be possible under high-pressure conditions to, in effect, create a new periodic table, wherein the ordinary chemical properties of the elements could be so changed that we would not recognize them.

Consider for a moment the periodic table shown in Fig. 2. In discussing the electronic structure of the various atoms, the terminology ordinarily applied to the free atom will

[1] Presented at the Symposium on High Pressures, Carnegie Institution Geophysical Laboratory, June 12, 1957. The author wishes to express his appreciation to the Carnegie Institution of Washington and the National Science Foundation for their financial support of the high-pressure research program at Brigham Young University.

[2] HALL, H. TRACY. Proceedings of a symposium, *High temperature—a tool for the future:* 161–166, 214–215. 1956. Published and distributed by Stanford Research Institute, Menlo Park, Calif.

be used. This will give qualitatively correct results.

In regard to the effect of high pressure on the elements, our first question arises with carbon, nitrogen, and oxygen, as we proceed with increasing atomic numbers through the periodic table. These elements contain unpaired "p" electrons. Can pressure force the "p" electrons with parallel spins into opposition, thereby decreasing the magnetic properties of these atoms? A like situation exists with respect to silicon, phosphorous, and sulphur. I think the answer is yes.

The second type of question arises with the element potassium, which has a vacant 3d shell. Should pressure force the 4s electron into this 3d orbital? This situation continues through nickel. All the elements underlined in Fig. 3 have empty "inner" orbitals and hence possess the possibility of forcing outer electrons at sufficiently high pressure into the empty orbitals,

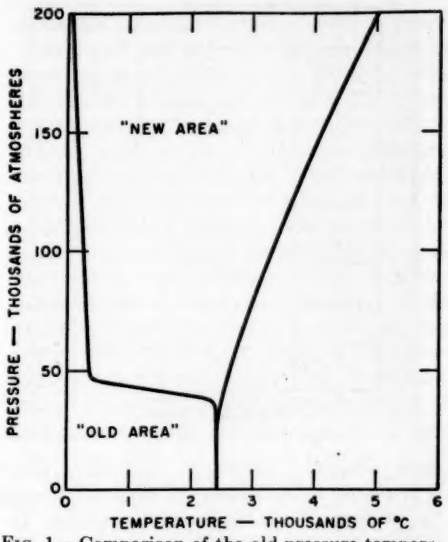

FIG. 1.—Comparison of the old pressure temperature region with the new region now available.

H																He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	A
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Cb	Mo	Ma	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	85	Rn
87	Ra	Ac	Th	Pa	U	Np	Pu	Am	Cm								
X	Ce	Pr	Nd	Il	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu			

FIG. 2.—Periodic chart of the elements. (Underlined elements have empty atomic orbitals.)

thereby changing the ordinary chemical properties of these materials. The underlined elements represent two-thirds of the periodic table. Again I think the answer is yes.

The element cesium occupies a unique and outstanding position in the periodic table, in that there are 6s, 5d, and 4f orbitals, which are very close together energywise; and in that there is but one outermost electron, which normally occupies the 6s orbital. Application of pressure to cesium metal offers the possibility of forcing this electron into the 4f position, thereby making the cesium a nonconductor. Additional application of pressure offers the possibility of pushing the electron into the 5d orbital, where the material would again become an electrical conductor, the increasing energy sequence of these orbitals being 6s, 4f, and 5d. Increasing pressure, injecting increasing amounts of energy into the system, would likely cause an electron to follow this energy sequence.

Fig. 3 shows the change in electrical resistance of cesium metal with increasing pressure.[3] At 53,200 atmospheres the electrical resistance increases very abruptly, as though the material were tending to become an electrical insulator. On increasing the pressure very slightly, the electrical resist-

[3] This phenomenon was first observed by P. W. Bridgman. Proc. Amer. Acad. Arts and Sci. **81**: 165–251. 1952.

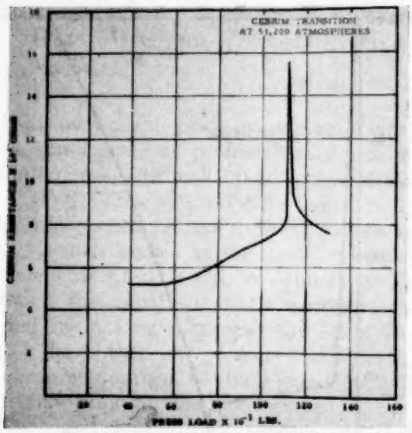

FIG. 3.—Cesium transition at 53,200 atmospheres.

ance abruptly decreases. Actually, there is probably a distribution of electrons among the various available energy positions. Investigation of this phenomenon at low temperatures might well establish the merits of the foregoing conclusions.

A common statement to be found in textbooks discussing nuclear phenomena is that radioactivity is not influenced by temperature or pressure. Of course, this statement is true when ordinary pressures and temperatures are involved. At pressures of the order of 200,000 atmospheres and above, however, it should be possible to affect some of the innermost electrons within atoms. It might well be possible that K capture, the phenomenon in which an electron from the K shell falls into the nucleus, should be effected at very high pressure conditions. Dr. S. S. Kistler and his associates at the University of Utah are presently studying this phenomenon.

In recent years man has plunged from a thorough study of the properties associated with the outermost part of atoms; i.e., the electrons, to a study of the innermost part, the nucleus. I have a hunch that there is an "in between world" waiting to be produced by application of extremely high pressures. In this world the normal electronic system would be displaced from its usual position to positions closer to the nucleus.

Let us now turn from these general electronic effects to some specific problems where high pressure might make a contribution. The field of geochemistry is ripe for exploitation with high-pressure, high-temperature techniques. This is true particularly in regard to the nature of the interior of the earth. Man's direct access to the earth's interior is, of course, very limited, the deepest excursions which he can personally make being limited to depths of about 1 mile (tunnels this deep are to be found in a South African gold mine). Oil wells have been drilled to depths of 4 miles, and, of course, instruments can be lowered to obtain information as to the nature of the earth at these depths.

Some very interesting thoughts on the nature of the core of the earth have recently been advanced by Dr. W. H. Ramsey.[4] In contrast to the usual view that the core is iron nickel with a silicate flux floating on top, Ramsey proposed that the core is composed of olivine which has been converted at the tremendous pressure of 1.4 million atmospheres to a metallic substance of density near 10. To support this theory Ramsey has studied the relationships existing among the planets in the solar system and has pointed out that the two smallest planets, Mars and Mercury, are not large enough to develop a pressure of 1.4 million atmospheres estimated necessary to support a core. Metallic and nonmetallic forms of elements are known in the laboratory. Gray tin is nonmetallic with a density of 5.75 g per cc. Application of pressure to gray tin will form a metallic white variety with a density of 7.28 g per cc. Arsenic has a yellow low-pressure modification of density 2.0 and a high-pressure metallic modification of density 5.73. Phosphorus has a low-pressure yellow form of density 1.82 and a high-pressure black from of density 2.70. E. Wigner and H. B. Huntington[5] have calculated that hydrogen could be transformed into a metallic form by application of pressures over 250,000 atmospheres.

Other geological problems can be answered by laboratory mineral synthesis at high of mineral synthesis in addition to its pressure and high temperature The field geological implications, can, of course, have

[4] Nature **168**: 667. 1951.
[5] Journ. Chem. Phys. **3**: 764–770. 1935.

industrial significance, as witness the recent synthesis of diamond and of cubic boron nitride. In the synthesis of minerals, it is desirable to use a catalyst or mineralizer. At high pressure and high temperature, all the oxides and silicates seem to have reasonable solubility in water. Therefore, water is probably the most important of the mineralizers. However, there is a long list of materials that can be used, which includes various salts, particularly those containing nitrogen, florine, carbon dioxide, and hydrogen. In the high-pressure equipment that I have used, it is possible to make the containing vessel or capsule of tantulum, nickel or other metal that readily passes hydrogen when the container is hot. It is, therefore, possible to allow for the continuous escape of hydrogen from a reaction, with the attendant decrease in volume.

Since high-pressure reactions are driven in the direction of decreasing volume, it is possible to almost always devise a scheme for synthesizing a desired product at high pressure and high temperature. For example, consider the following reaction for the synthesis of aluminum oxide:

$$\underbrace{2\,AlCl_3 + 2Fe + 3H_2O}_{V = 305\ cm^3} \rightarrow \underbrace{Al_2O_3 + 2FeCl_3}_{V = 131\ cm^3} + 3H_2\uparrow$$

Since high pressure tends to reduce "open" structures to closer packed structures and strives to arrange atoms in positions of maximum three-dimensional symmetry, any system not in cubic or hexagonal close packing is a worthy object of study at high pressure and high temperature, for here the possibility exists of producing a higher density system.

The synthesis of hard materials might be considered at this point. Hardness is a property resulting from high bond density and from high three-dimensional symmetry. A measure of high bond density is the so-called cohesive energy density. A measure of cohesive energy density is the heat of vaporization of a material per cubic centimeter. When such information is not available, a relative measure of bond density can be obtained by dividing the boiling point of a substance by its molar volume. Graphite and diamond have the highest cohesive energy densities of any known materials. Graphite, however, is soft, whereas the diamond is the hardest of all known substances. The reason for this is that graphite does not fulfill the second requirement of high 3-dimensional bond symmetry. Carbides, nitrides, borides, oxides, and sulphides of elements in the neighborhood of carbon and silicon, together with some of the heavy metals of the periodic table, have high cohesive energy densities. Some of these materials produced under ordinary conditions do not have high bond symmetry. Since high pressure tends to force bonds into positions of highest 3-dimensional symmetry, the application of high pressure and high temperature to some of these materials can result in the production of hitherto unknown materials of very high hardness. The recent synthesis of "borazon" by Dr. R. H. Wentorf, Jr., of the General Electric Research Laboratory is an example of this situation.

I think there are some excellent prospects in the field of metallurgy for experimental work at high pressure and high temperature. It is well known that the calculated yield strengths of many metals are 100 to 10,000 times greater than those measured. Yield strength is a structure-sensitive property; that is, the strength is dependent on the existence of vacant sites, dislocations, small- and large-angle boundaries, etc. The elimination of vacant sites, etc., would result in an improvement of the yield strength of metals. This elimination would also result in a volume decrease in the material; and since the application of high pressure tends to drive things in the direction of decreasing volume, such application might prove beneficial. There are undoubtedly activation barriers opposing the removal of the above. These barriers could be reduced by use of high temperature and catalysts (fluxes); and hence the necessary eliminations could be carried out at a reasonable rate.

Most metallic materials are polycrystal-

line. This is another factor causing lower than calculated yield strengths. Of course, single crystals would have a smaller volume than polycrystals, since the density of the grain boundaries is about ten per cent less than that of the grains. There is also a certain amount of free energy associated with the grain boundaries. Application of high pressures would favor the elimination of grain boundaries and the growth of single crystals from polycrystals.

The heat treatment of metals is an indispensable process carried out in our modern industrial economy. The formation of desirable properties in metals by heat treatment is, in general, brought about by heating a material, for example, steel, to a rather high temperature, at which temperature certain transformations take place. The material is then quenched (rapidly cooled) to a lower temperature. This quenching produces certain desirable structures in the material. Temperature, then (for fixed composition), has been the only variable the metallurgist has had at his command. Certainly, pressure could be introduced as a variable, and as an example, the following sequence might be followed in producing certain desired properties in a metal: (1) The metal is heated at 1 atmosphere pressure to a certain temperature; (2) high pressure is now applied to the metal; (3) the temperature is lowered; and (4) the pressure is lowered. This sequence of events could conceivably "lock-in" properties that could be obtained in no other way.

High pressure could offer a new crystallization technique. Normally, metals are produced from the melt by cooling. Metals could be crystallized from a melt by leaving the temperature constant and increasing the pressure. In multi-component systems, this might produce some unusual results.

At the present time, the volume of material that can be subjected to high pressure and high temperature is rather small, practical size being not greater than a few cubic centimeters. For commercial application, this requires that the material made at high pressure be quite valuable. Two categories of material come to mind that fit this classification: They are diamonds, or other materials of comparable hardness, and drugs, or other biological materials. It is quite possible that some directed, tricky substitutions in complicated molecules of biological importance could be brought about by application of pressure that could be achieved in no other way.

The melting points of substances are profoundly affected by pressures of the order of 200,000 atmospheres. For example, note the 600° lowering of the melting point recently reported.[6] Of course, germanium is an exception to the general rule that melting point increases with increasing pressure. The melting point of some refractory materials has been increased by well over 1,000°C. by the application of extremely high pressures. This fact makes it possible to work at higher temperatures at high pressure than would be possible at one atmosphere. As a matter of fact, it is quite possible to work with a "liquid" refractory under high pressure conditions. A liquid can flow only if it contains holes into which the molecules can move. At 200,000 atmospheres, the number of holes in a molten refractory can be severely reduced, and the material will be extremely viscous.

Work on the melting points of substances at high pressure has considerable significance, in that it should throw some light on the old question as to the possible existence of a critical point between liquid and solid analogous to the critical point between a gas and a liquid.

High pressure increases the electrical conductivity of most metals by approximately 20 percent at 100,000 atmospheres. However, the conductivity of some metals is increased by as much as 400 percent. This phenomenon, of course, falls in line with the fact that, in general, high pressure behaves like low temperature. This raises the question: Is superconductivity possible at sufficiently high pressure?

Certainly, many applications of high pressure at low and high temperatures are to be found in atomic and molecular theory, geology, chemistry, physics and other scientific disciplines.

[6] HALL, H. T. Journ. Phys. Chem. **59**: 1144. 1955.

PALEONTOLOGY.—*Notes on the ostracode subfamily Cytherideidinae Puri, 1952.* HARBANS S. PURI, Florida Geological Survey. (Communicated by Alfred R. Loeblich, Jr.)

(Received April 9, 1957)

The subfamily Cytherideidinae was proposed by Puri (1952, pp. 905–906) to include *Cytherideis* Jones, 1857; *Copytus* Skogsberg, 1939; *Pontocythere* Dubovsky, 1939; *Krithe* Brady, Crosskey and Robertson, 1874; *Cushmanidea* Blake, 1933; *Sahnia* Puri, 1952; and *Neocytherideis* Puri, 1952. *Cytherideis* Jones, 1857, was chosen as the type genus for this subfamily (hence the name Cytherideidinae) because of its widespread and established usage, although it was realized that the validity of this genus was doubtful since it did not satisfy the requirements of the International Commission on Zoologic Nomenclature. Jones (1856) first published the name *Cytherideis* for two species of Ostracoda from the Tertiary of the Isle of Wight. Since Jones did not give generic diagnosis, publication of this new genus would be considered to be invalid (Opinion 1, International Commission on Zoologic Nomenclature) and the genus predated to Jones's 1857 publication in which he actually described it as new and gave generic diagnosis. *Cytherideis* thus was interpreted as described and figured by Jones in 1857. However, the International Commission on Zoologic Nomenclature rescinded Opinion 1 (Hemming, 1950, pp. 78–80) and this genus should once again date back to 1856. Since Sylvester-Bradley and Harding (personal communication, February 1952) planned to petition the International Commission on Zoologic Nomenclature to use plenary powers to validate this otherwise invalid genus, Puri (1952) continued the usage of this name. Later, Sylvester-Bradley and Harding (1953) withdrew their application and designated one of the two species (*Cytherideis unicornis*) described by Jones in 1856 as the type species. This species actually belongs to *Cypridea* Bosquet, thus *Cytherideis* Jones becomes a synonym of *Cypridea* Bosquet and the subfamily Cytherideidinae a synonym of the subfamily Cyprideinae. This leaves nameless the taxonomic unit intended to include "*Cytherideis*" and its allied group.

Consequently, the following nomenclature is here proposed for the "Cytherideidinae":

Order OSTRACODA Latreille
Suborder PODOCOPA Sars
Family CYTHERIDAE Baird
Subfamily Neocytherideidinae Puri, n. name (= Cytherideisinae Puri, 1952; Cytherideidinae (Puri) Sylvester-Bradley and Harding, 1953). Type genus, *Neocytherideis* Puri, 1952. Type species, *N. elongatus* Puri = *Cytherideis subulata fasciata* Brady and Robertson, 1874.
Genus *Sahnia* Puri, 1952. Type species, *Cytherideis subulata* Brady of Puri, 1952.
Genus *Krithe* Brady, Crosskey, and Robertson, 1874. Type species, *Ilyobates pretexta* Sars, 1865 (1866) = *Cytherideis bartonensis* Jones, 1857.
Genus *Copytus* Skogsberg, 1939. Type species, *C. caligula* Skogsberg.
Cytherideis of authors.
Hemicytherideis Ruggieri, 1952 (type species, *Cytheridea elongata* Brady, 1868).
?Cushmanidea Blake, 1933 (type species, *Cytheridea seminuda* Cushman, 1906).
Genus *Pontocythere* Dubovsky, 1939.
Type species, by monotypy *P. tchernijawskii* Dubovsky, 1939.

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PALEONTOLOGY.—Postscript notes on the ostracode subfamily Brachycytherinae.

HARBANS S. PURI, Florida Geological Survey. (Communicated by Alfred R. Loeblich, Jr.)

(Received April 9, 1957)

The subfamily Brachycytherinae was erected by Puri (1954, p. 248) to include *Brachycythere* Alexander (1933, p. 204) and *Alatacythere* Murray and Hussey (1942, pp. 169–171). Murray and Hussey (op. cit.) designated *Cythereis* (*Pterygocythereis?*) *alexanderi* Howe and Law (1936, pp. 42, 43) as the type species of *Alatacythere*. Howe (1951, p. 538) proposed a new name, *ivani*, for the type species since it was found to be preoccupied by *Cythereis alexanderi* Morrow (1934, p. 203). *Alatacythere* as conceived by Murray and Hussey (op. cit.) consisted of two groups with radically different types of hinges. The first group, typified by *Cythereis alexanderi*, has a trachyleberid-type hinge; the second group, with species like *Cypridina alata* Bosquet (1847, p. 369), has a *Brachycythere*-type hinge. Since Murray and Hussey also included species with *Brachycythere*-type hingement under *Alatacythere*, Puri (1954, p. 248) placed this genus under Brachycytherinae. Because part of *Cypridina alata* Bosquet of Murray and Hussey was not conspecific with Bosquet's species, Hill (1954, p. 822) proposed a new specific name *Pterygocythere murrayi* for its reception. Further, Hill (op. cit., pp. 819–820) erected a new genus, *Pterygocythere*, with *P. murrayi* as its type species and included under it forms with a *Brachycythere*-type hinge formerly included in *Alatacythere*. The other group of species (with a trachyleberid hinge) originally included by Murray and Hussey under *Alatacythere*, are now included by Hill (1954) under *Pterygocythereis* Blake. This procedure, if followed, would make *Alatacythere* an invalid genus.

Taxonomically, *Alatacythere* is a valid genus, but its use should be restricted to only those species which show the hingement encountered in the type species, *A. ivani*. The hinge in the type species in the right valve consists of an anterior rounded tooth, a postjacent socket that connects with the posterior crenulate tooth through a deep furrow. This deep furrow is bound dorsally and ventrally by parallel flanges. *Pterygocythereis* on the other hand has both the anterior and the posterior elements of the hingement crenulate in the molt stages only; the adult never shows any crenulations of the teeth and the hingement basically is of *Trachyleberis*-type.

As a practical solution to this confused problem, two different subfamilies are provided to accommodate "winged" forms with *Brachycythere*-type hinge structure and "winged" genera with trachyleberid hinge. *Alatacythere* is redefined and restricted to species which have the same hingement as the type species.

SYSTEMATIC TREATMENT

Order OSTRACODA Latreille

Suborder PODOCOPA Sars

Family TRACHYLEBERIDAE Sylvester-Bradley

PTERYGOCYTHERINAE, Puri, n. subfam.

Type genus: *Pterygocythereis* Blake, 1933.

Carapace pellucid, fragile, broadly triangular, with prominent ventrolateral wings. Hingement essentially *Trachyleberis*-type, valve articulate by means of terminal teeth, sockets, grooves and flanges.

This subfamily comprises the following genera: *Pterygocythereis* Blake and *Alatacythere* Murray and Hussey.

Genus **Pterygocythereis** Blake, 1933

Fimbria Neviani, 1928, pp. 72, 86 (not *Fimbria* Rosso, 1826).

Type species: Cythereis jonesi Baird, 1850, p. 175, pl. 20, fig. 1.

Carapace pellucid, fragile, hyaline, subtriangular, alate, with two well-developed ventrolateral wings. Muscle scar pattern consists of a vertical row of four scars and a U-shaped scar in front of the vertical row. Hinge in the right valve with a smooth anterior tooth, a postjacent socket leading to a posterior smooth, triangular tooth through a straight groove. This groove is bound dorsally and ventrally with flanges. Hinge of the left valve complementary. In the molt stages both the anterior and the posterior elements of hingement are crenulate.

Range: Cretaceous to Recent.

Remarks: Fimbria Neviani, 1928, is an earlier name for this group, but it is preoccupied and not available. The sole species referred to *Fimbria* by Neviani (*Cythere fimbriata* Münster) is synonymous with *Cythereis jonesi* Baird, the type of *Pterygocythereis* (Lienenklaus, 1894, p. 216; Key, 1955, p. 129).

Genus **Alatacythere** Murray and Hussey, 1942 (emended)

Type species: Cythereis (*Pterygocythereis?*) *alexanderi* Howe and Law, 1936, pp. 42, 43, pl. 4, fig. 23; pl. 5, fig. 5, (not *Cythereis alexanderi* Morrow, 1934, p. 203, pl. 31, figs. 14a–c) = *Alatacythere ivani* Howe (1951, p. 538) n. name.

Carapace pellucid, fragile, subtriangular, alate with well-developed ventrolateral wings. Muscle scar pattern in the type species consists of a group of three scars above a vertical row of four scars; in front of the ventral scar there is another scar. Hinge in the right valve with an anterior, large, rounded tooth, a postjacent socket connecting with the posterior large crenulate tooth through a straight groove. This groove is bound both dorsally and ventrally by flanges that parallel the grove

Range: Oligocene.

Family CYTHERIDAE Baird, 1850

Subfamily BRACHYCYTHERINAE Puri, 1954 (emended)

Type genus: *Brachycythere* Alexander, 1933, p. 204.

Carapace subquadrate to subovate, surface smooth, pitted or reticulate, inflated ventrally with a well-developed ala or a ventrolateral wing. Hingement essentially crenulate, valves articulate by means of terminal crenulate teeth, sockets and median and/or dorsal and ventral crenulate grooves and dorsal and ventral and/or dorsal, median and ventral hinge-bars. Anterior elements of the hingement in intermediate genera are noncrenulate. Line of concrescence and inner margin coincide.

This subfamily includes the following genera: *Brachycythere* Alexander, *Pterygocythere* Hill, and *Diogmopteron* Hill.

Genus **Brachycythere** Alexander, 1933

Type species: Cythere sphenoides Reuss, 1854, p. 141, pl. 26, fig. 2.

Carapace large, subquadrate to subovate; valves inequal (left larger than right). Anterior end broadly and obliquely rounded; posterior end narrower than the anterior and compressed. Both dorsal and ventral margins arched. Surface of the carapace smooth, pitted or reticulate. Carapace inflated with a well-developed ala. Hinge in the right valve with an anterior crenulate tooth, a postjacent socket leading to the posterior crenulate tooth, through a groove. This groove is bound dorsally and ventrally by hinge-bars. Hinge of left valve complementary. Muscle scar pattern consists of a vertical row of four scars; in front of this vertical row is another vertical row of two scars; the upper one is heart-shaped; anterior to the second vertical row, there is another heart-shaped scar. Marginal areas are broad, radial pore canals are numerous, and closely spaced with a tendency to branch in the

anteroventral region. Line of concrescence and the inner margin coincide.

Range: Cretaceous to Recent.

Genus **Pterygocythere** Hill, 1954

Type species: Cypridina alata Bosquet, 1847, p. 369, pl. 4, figs. 1a–d.

Carapace large, subquadrate to subovate. Anterior end compressed, broadly and obliquely rounded; posterior end compressed and narrower than the anterior. Dorsal margin arched; ventral margin nearly straight. Surface of the carapace smooth or spinose, carapace alate, with well-developed ventrolateral wing. Hinge in the right valve with a crenulate anterior tooth, a postjacent socket leading to the large, elongate, crenulate, posterior tooth through a groove. This groove is bound both dorsally and ventrally by hinge-bars. Hinge of the left valve complementary. Marginal areas are broad, radial pore canals numerous, irregular, closely spaced. Line of concrescence and inner margin coincide.

Range: Upper Cretaceous to Oligocene.

Remarks: This genus can be easily distinguished from *Brachycythere* by its ventrolateral wing. It could be separated from *Pterygocythereis*, which it resembles externally, by its *Brachycythere*-type hinge. *Pterygocythereis* has a characteristic *Trachyleberis*-type hinge.

Genus **Diogmopteron** Hill, 1954

Type species: Brachycythere lünenensis Triebel, 1941, pp. 383–385, pl. 8, figs. 77–80.

Carapace small to medium, subquadrate. Anterior end broadly and obliquely round, posterior end narrower and compressed. Dorsal margin nearly straight; dorsal and ventral margins converge posteriorly. Surface of the carapace smooth or spinose. Carapace alate, with a well-developed ventrolateral wing. Hinge in the right valve with a smooth anterior tooth, a postjacent socket leading toward the posterior crenulate tooth through a groove. Both dorsally and ventrally this groove is bound by hinge-bars. Above the dorsal hinge-bar, there is another groove which roughly parallels the dorsal hinge-bar and is bounded dorsally by another hinge-bar. Line of concrescence and inner margin coincide. Muscle scar pattern consists of four scars arranged in the shape of an inverted "L".

Range: Upper Cretaceous.

Remarks: This monotypic genus is fundamentally a *Brachycythere* except for having two grooves (dorsal and ventral) and three hinge-bars (dorsal, median and ventral). *Brachycythere* exhibits only one such groove and two hinge-bars.

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MYCOLOGY.—*Two medium-sized species of* Conidiobolus *occurring in Colorado.* CHARLES DRECHSLER, Crops Research Division, Agricultural Research Service, United States Department of Agriculture.

The two readily culturable entomophthoraceous fungi herein described as new species of *Conidiobolus* were obtained by canopying Petri plates of maize-meal agar with moist filter paper to which had been securely affixed minute quantities (0.03 to 0.05 gram) of decaying plant detritus kindly gathered by W. J. Zaumeyer near Greeley, Colo., in August 1956. Dried portions of Petri plate cultures of the two fungi have been deposited in the National Fungus Collection, Beltsville, Md.; although, unfortunately, the morphological features distinguishing the readily culturable members of the Entomophthorales are for the most part not well revealed in such desiccated material.

1. **Conidiobolus denaeosporus** sp. nov. Mycelium paene omnino in materia alimentaria immersum, parce in aerem assurgens, itaque aliquid inconspicuum; hyphae steriles filiformes, ramosae, rectae vel pravae, vulgo passae sed interdum in pabulo validissimo dense intertextae, plerumque 2.5–10 μ crassae, mox septatae, postea hic illic disjunctae vel inanitae, cellulae eorum plerumque 25–250 μ longae, primo incoloratae, in senio aliquanto sufflavae; primiformes fertiles hyphae singulatim ex cellulis hypharum surgentes, simplices, in aerem saepe 15–50 μ ad lucem protendentes, in parte aeria erectae vel acclives, illic plerumque 4–7.5 μ crassae, apice unum conidium ferentes; primiformia conidia violenter absilientia, saepius in pulverem album visibilem accumulata, primo incolorata, postea in senio aliquid subflava, paulum perdurantia, globosa vel saepius turbinea, apice late rotundata, deorsum in papillam 4–7.5 μ latam et 2–6 μ altam abeuntia, ex toto 13–32 μ longa, 6–21 μ crassa; graciles fertiles hyphae singulatim ex primiformibus vel secundariis conidiis surgentes, incoloratae, simplices, 35–65 μ longae, basi 1.5–3 μ latae, sursum leniter attenuatae, apice circa 1 μ latae, ibi unum secundarium conidium ferentes; secundaria conidia incolorata, elongato-ellipsoidea, 10–18 μ longa, 6–10 μ lata.

Habitat in foliis *Ulmi parvifoliae* putrescentibus prope Greeley, Colorado.

Mycelium almost wholly intramatrical, with little or no aerial development, and thus rather inconspicuous; vegetative hyphae filamentous, branched, almost straight or variously crooked, for the most part spreading out uniformly but in highly nourishing morsels often closely interwoven, mostly 2.5 to 10 μ wide, early divided by cross-walls; the resulting hyphal segments mostly 25 to 250 μ long, often disjointing or becoming separated by portions of emptied membrane, always colorless when young but later sometimes turning yellowish; primary conidiophores arising singly from submerged or prostrate hyphal segments, extending 15 to 50 μ into the air toward the main source of light, in the aerial portion erect or inclined, 4 to 7.5 μ wide, bearing a single primary conidium; primary conidia springing off forcibly, often accumulating in whitish deposits visible to the naked eye, relatively long-lived, always colorless when young but when old sometimes yellowish, globose or more often turbinate with spherically rounded distal end and somewhat obconical proximal end, measuring 6 to 21 μ in greatest width and 13 to 32 μ in length inclusive of a basal papilla 4 to 7.5 μ wide and 2 to 6 μ high; slender conidiophores arising singly from globose primary or elongated secondary conidia, colorless, unbranched, 35 to 65 μ long, 1.5 to 3 μ wide at the base, tapering gradually upward, about 1 μ wide at the tip, there bearing a single secondary conidium; secondary conidia colorless, elongate-ellipsoidal, 10 to 18 μ long and 6 to 10 μ wide.

Isolated from decaying leaves of *Ulmus parvifolia* Jacq. collected near Greeley, Colorado.

The main hyphae at the margin of an actively growing mycelium of *Conidiobolus denaeosporus* commonly measure about 7 μ in width and usually terminate in a distal segment (Fig. 1, A) 125 to 250 μ long. As each distal segment pushes forward at the tip it successively cuts off shorter segments, mostly 25 to 100 μ long, at its proximal end. The hyphal segments thus delimited later often undergo changes in shape through emission of lateral branches. In Petri plate cultures of soft agar containing finely divided maize-meal the lateral branches may attain rather extensive

development, and are usually distinguished by conspicuous irregularity of outward form (Fig. 1, B, C). Within and around the larger deposits of maize-meal the branches may become closely interwoven into irregular masses of prosenchyma.

When *Conidiobolus denaeosporus* is well nourished it soon shows abundant asexual reproduction. The numerous phototropic conidiophores (Fig. 1, D–I) then formed, as also the globose or turbinate conidia (Fig. 1, J, a–w) springing off from them, more closely resemble in shape and dimensions the corresponding reproductive structures of *C. rugosus* Drechsler (1955) than those of any other known congeneric form. As might be inferred from the relative size of the basal papilla the conidium commonly springs off with at least moderate force; so that in many instances it falls on unoccupied substratum beyond the limits of the parent mycelium, and thus can readily germinate vegetatively to form a subsidiary mycelium. Accordingly in Petri plate cultures receiving light mainly from one side the fungus spreads more rapidly and disconnectedly toward the source of illumination than in other directions.

Among the numerous globose or turbinate conidia that are found strewn about thickly after asexual reproduction has been proceeding for several days, some scattered individuals are nearly always found giving rise on broad phototropic outgrowths to single conidia (Fig. 1, K–P) which in their turn spring off forcibly. This purely repetitional development begins early and continues for weeks, though usually it proceeds less abundantly than in related species. The emission from globose conidia of slender conidiophores (Fig. 1, Q–S) bearing ellipsoidal secondary conidia (Fig. 1, T, a–o) is not commonly observable in cultures much under 10 days old. Once initiated the latter type of sporulation usually continues for several weeks, even if, for the most part, only rather sparingly. All the globose or turbinate conidia that so far have been observed giving rise to elongated secondary conidia have been of relatively small size. Should some of the larger globose conidia participate in such sporulation the resulting elongated secondary conidia might be expected to exceed the dimensions given in the diagnosis.

Multiplicative reproduction by the formation of microconidia extended plurally from globose conidia has not hitherto been observed in the several isolations of *Conidiobolus denaeosporus*. None of the isolations has shown any development of chlamydospores. In all series of cultures the several isolations have failed to show sexual reproduction, although cultures of *C. rugosus* on the same medium that were inoculated at the same time and kept at the same temperature consistently formed zygospores in large numbers.

It seems probable that *Conidiobolus denaeosporus* survives unfavorable periods mainly in its globose or turbinate conidia, as these appear considerably more durable than the homologous spores of most congeneric species. In young cultures they are commonly filled throughout with protoplasm that is partly of homogeneous and partly of granular texture (Fig. 1, J, a, f, l–o, q, t). After 60 days they usually show a conspicuous vacuole (Fig. 1, J, b-e, h–k), but their protoplasm, though of diminished volume, remains fully alive, often in Petri plate cultures, despite the presence of alien molds usually ruinous to the asexual spores of some other members of the genus. Similarly vacuolated living conidia (Fig. 1, J, p, s) are usually still abundant in tube cultures 4 months old. When conidia from a nearly dried maize-meal-agar culture 6 months old are moistened a large proportion of them promptly show unmistakably live protoplasm of lumpy texture in a parietal layer surrounding a large central vacuole (Fig. 1, J, u–w). The specific epithet compounded of two words (*δηναιος*, *σπορος*) meaning "long-lived" and "seed", respectively, is intended to signalize the rather exceptional endurance of the conidia.

A yellowish coloration often noticeable in vacuolated conidia from maize-meal-agar tube

FIG. 1.—*Conidiobolus denaeosporus* as found in maize-meal-agar cultures; all parts drawn at a uniform magnification with the aid of a camera lucida; × 1000. A, Terminal portion of hypha at forefront of a growing mycelium. B, C, Irregular hyphal segments near center of a mycelium in a culture 10 days old. D, Distal portion of phototropic conidiophore with conidium nearly ready to be completely delimited; s, surface of substratum. E–I, Phototropic conidiophores, each bearing a fully delimited conidium; s, surface of substratum. J, Detached globose conidia, a-w, from culture 4 days to 6 months old, showing usual variations in size, shape, and internal structure. K-P, Globose conidia, each with a stout phototropic outgrowth bearing another globose conidium. Q-S, Globose conidia that have each sent up a slender conidiophore bearing an elongated conidium. T, Fifteen elongated conidia, a-o, showing usual variations in size and shape. U, Indurated distal portion of a conidiophore found in culture 6 months old.

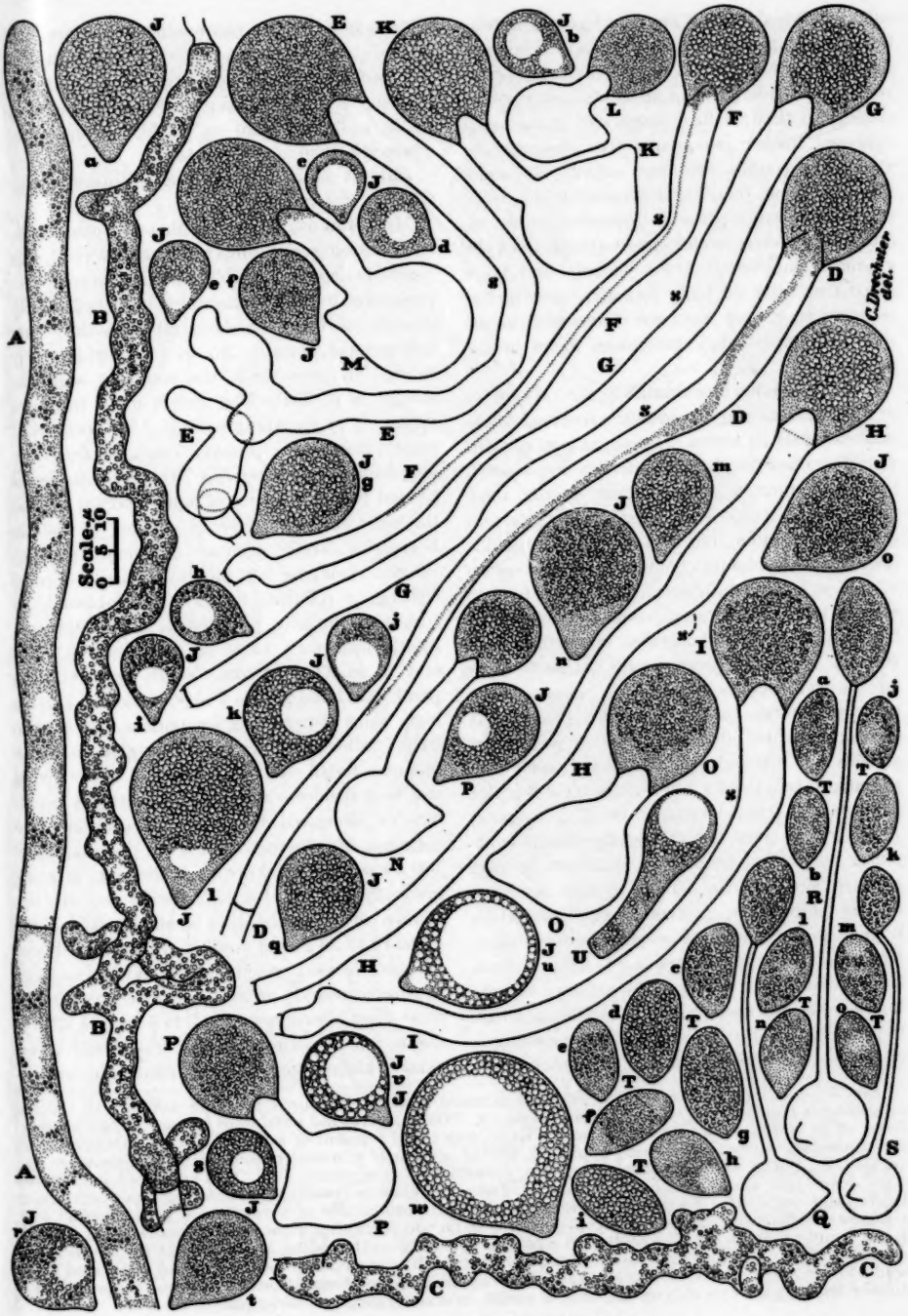

FIG. 1.—(See opposite page for explanation).

cultures several months old may have some relation to the durable character of the spores. Similar coloration permeates also the living segments of vegetative hyphae and of abortive conidiophores (Fig. 1, U) that are likewise present in the aging cultures. Rather commonly the pronouncedly vacuolated conidia are more rotund and wider (Fig. 1, J, u–w) than newly formed conidia, some of them exceeding 26 μ in diameter. As the increase in diameter would seem to result from the gradual enlargement of the vacuole, and takes place long after all truly formative growth has come to an end, it has been disregarded in the statement on conidial dimensions given in the diagnosis.

2. **Conidiobolus inordinatus** sp. nov. Mycelium in materia alimentaria immersum, fere oculo nudo non visibiliter in aerem crescens, et non conidiis visibiliter tectum; hyphae steriles incoloratae, filiformes, ramosae, nunc paene rectae nunc valde pravae, vulgo aliquid inordinatae, plerumque 2.5–10 μ latae, mox septatae, postea hic illic disjunctae vel inanitae, cellulae viventes eorum 10–250 μ longae; primiformibus fertiles hyphae aliquid rarae, incoloratae, simplices, ex cellulis hypharum singulatim surgentes, in aerem saepius 20–60 μ ad lucem protendentes, in parte aeria erectae vel acclives, hic 4–9 μ crassae, apice unum primiforme conidium ferentes; primiformia conidia violenter absilientia, parca, incolorata, globosa vel obovoidea vel turbinea, apice late rotundata, basi papilla 4–9 μ crassa et 3–6 μ alta praedita, ex toto plerumque 15–32 μ longa et 12–25 μ lata, nunc hypham germinationis emittentia nunc aliud primiforme conidium ferentia nunc in apice gracilis fertilis hyphae conidium formae ellipsoideae gignentia; graciles fertiles hyphae incoloratae, saepe prope apicem curvatae, 50–100 μ longae, basi circa 2.5 μ latae, sursum leniter attenuatae, apice 1–1.5 μ latae; conidia formae ellipsoideae incolorata, 15–26 μ longa, 9–13 μ lata; chlamydosporae in hyphis submersis et procumbentibus copiose et festinanter ortae, saepius inordinatae, plerumque intercalares vel aliquid laterales, cylindratae vel globosae vel elongato-ellipsoideae vel bisulcae vel aliquid trifidae, incoloratae, saepius 20–36 μ longae et 12–20 μ latae, vulgo ex parte magna protoplasmatis globuliferi repletae.

Habitat in foliis *Ribis* putrescentibus prope Greeley, Colorado.

Mycelium usually with little or no macroscopically visible aerial growth and not overlaid with conidial deposits visible to the naked eye; vegetative hyphae filamentous, branched, nearly straight or often crooked, often in disorderly arrangement, mostly 2.5 to 10 μ wide, early divided by cross-walls, the resulting segments mostly 10 to 250 μ long and in many instances disjoining or becoming separated by portions of empty membrane; primary condiophores colorless, unbranched, extending 20 to 60 μ into the air toward the main source of light, 4 to 9 μ wide in the erect or inclined aerial portion, at the tip bearing a single primary conidium; primary conidia springing off forcibly, usually formed sparingly, colorless, globose or obovoid or turbinate, broadly rounded at the distal end, mostly measuring 12 to 25 μ in greatest width and 15 to 32 μ in total length inclusive of a paraboloid basal papilla 4 to 9 μ wide and 3 to 6 μ high, some germinating by putting out a germ hypha, others producing another globose conidium on a broad outgrowth, and still others giving rise to a slender condidiophore bearing a conidium of elongated type; slender conidiophores colorless, often somewhat curved distally, 50 to 100 μ long, about 2.5 μ wide at the base, tapering gradually upward, 1 to 1.5 μ wide near the tip; conidia of elongated type colorless, ellipsoidal, often 15 to 26 μ long and 9 to 13 μ wide; chlamdospores formed on submerged and procumbent hyphae, produced promptly and very copiously, most often intercalary with 2 to 4 hyphal attachments but sometimes lateral or laterally intercalary, globose or elongated-ellipsoidal or cyl-

FIG. 2.—*Conidiobolus inordinatus* as found in maize-meal agar cultures; all parts drawn with the aid of a camera lucida at a uniform magnification; × 1000. A, Terminal portion of a main hypha at forefront of an actively growing mycelium. B, Relatively small segment of a lateral branch extended from an intercalary segment of a main hypha. C, Distal portion of a lateral branch with a pronounced distention. D, Young phototropic conidiophore; s, surface of substratum. E, F, Two conidiophores almost fully developed; s, surface of substratum. G, Detached globose conidia, a–z, showing usual variations in size and shape. H, Globose conidium germinating by production of a vegetative germ hypha. I–K, Globose conidia, each with a phototropic outgrowth on which another globose conidium is being formed. L, M, Empty globose conidia, each with a phototropic outgrowth bearing a new globose conidium ready to spring off. N, O, Empty globose conidia, each with a slender conidiophore bearing an elongated ellipsoidal conidium. P–R, Detached elongated conidia showing usual variations in size and shape. S, Portion of hypha with two chlamydospores, a and b, in a completed or nearly completed state.

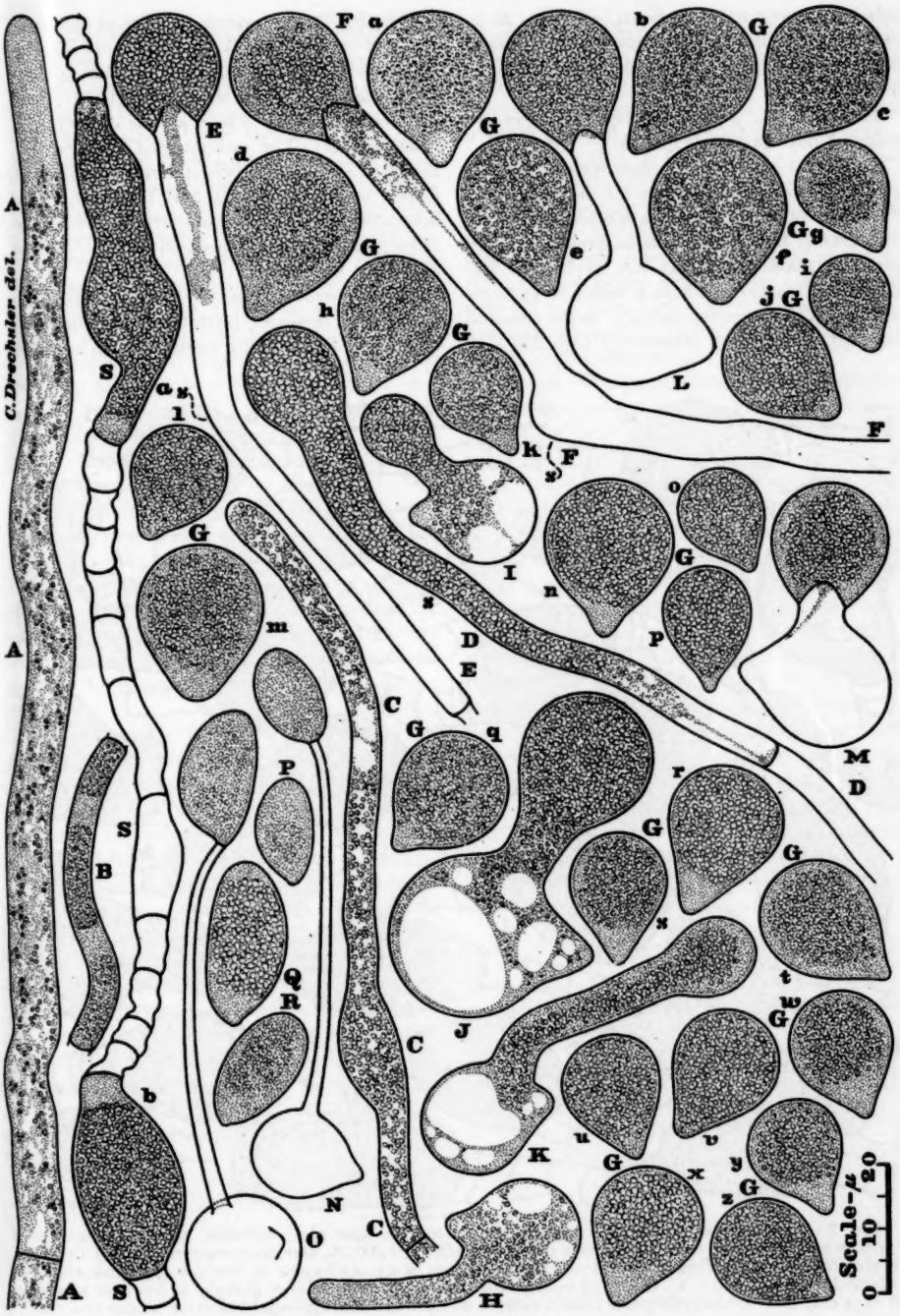

FIG. 2.—(See opposite page for explanation).

indrical or irregularly lobulated, colorless, 20 to 36 μ long, 12 to 20 μ in greatest width, usually fiilled in large part with strongly globuliferous protoplasm.

Isolated from decaying leaves of *Ribes* sp. collected near Greeley, Colorado.

In comparison with the other members of the genus, *Conidiobolus inordinatus* may like *C. denaeosporus* be considered a species of medium dimensions. When its mycelium grows in a Petri plate of maize-meal agar the hyphae at the advancing margin maintain a width of approximately 7 μ in elongating apically. As the terminal segment, which often measures 175 to 250 μ in length (Fig. 2, A), pushes forward at the tip it cuts off proximally a succession of shorter segments mostly between 25 and 125 μ long. From many of these shorter segments lateral branches commonly 3 to 6 μ wide are extended promiscuously. The intermingled ramifications, in which are included cells differing greatly with respect to size, shape (Fig. 2, B, C; Fig. 3, A) and orientation, contribute to a characteristic disorderly appearance signalized in the epithet applied to the species.

In maize-meal agar cultures *Conidiobolus inordinatus* produces phototropic conidiophores (Fig. 2, D–F) for many weeks, though as a rule

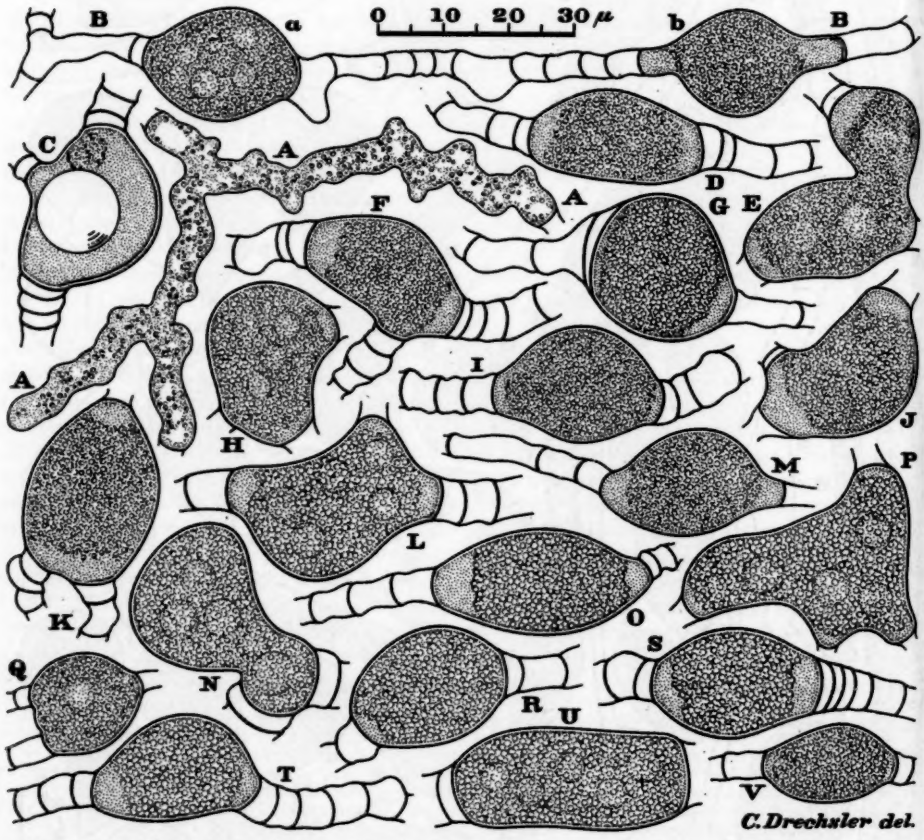

FIG. 3.—*Conidiobolus inordinatus* as found in maize-meal-agar plate cultures; all parts drawn at a uniform magnification with the aid of a camera lucida; × 1,000. A, Irregular segment formed in an extensive branch originating from an intercalary segment of a main hypha. B, Portion of hypha with two chlamydospores, a and b. C. Chlamydospore with large vacuole, or reserve globule, as found in a culture 55 days old. D–V, Chlamydospores from a culture 8 days old, showing usual variation in size and shape.

only rather sparingly. Its conidia (Fig. 2, G, a–z) never were found in such abundance as to be visible collectively to the naked eye. Under a microscope they commonly appear scattered somewhat sparsely over the substratum. On fresh unoccupied substratum the detached conidium may germinate by putting forth a vegetative germ hypha (Fig. 2, H). Often, however, on fresh unoccupied substratum, and also very commonly on substratum already overgrown by the fungus, the detached conidium puts forth a broad phototropic outgrowth (Fig. 2, I–K) on which another globose conidium is formed (Fig. 2, L, M). Cultures well over 10 days old usually show some relatively small globose conidia that have germinated by sending up a slender conidiophore supporting an elongated conidium (Fig. 2, N, O). As in related species the elongated ellipsoidal conidia here (Fig. 2, P–R) becomes detached on slight disturbance. They usually show more pronounced curvature on one side than on the other. Generally they reveal a somewhat oblique basal hilum that is nearly in alignment with the contour of the more strongly curved side. If the larger globose conidia were to serve as parents the elongated conidia then produced could be expected to exceed the dimensions given in the diagnosis.

The outstanding feature of *Conidiobolus inordinatus* is its early and remarkably copious production of chlamydospores (Fig. 2, S; Fig. 3, B-V). Even in cultures only a few days old its disorderly mycelium becomes so abundantly septate and discontinuous that on casual examination the fungus would not ordinarily be taken for a phycomycete. Local swellings representing early stages in chlamydospore development can often be recognized in hyphal segments only 2 to 3 millimeters from the forefront of a growing mycelium. As protoplasmic materials are gathered into the swellings the adjacent portions of hypha are progressively evacuated of contents. Retaining walls are laid down, one after another, at successive stages of this evacuation. These later appear as convex partitions in the emptied portions of tubular membrane, often 50 to 100 μ in length, between neighboring chlamydospores (Fig. 2, S, a, b; Fig. 3, B, a, b). Since in many instances chlamydospores are produced in positions where a hypha gives off 1 or 2 branches it often is supplied from 3 (Fig. 3, C, E, F, H, J–L, Q) and sometimes is supplied from 4 hyphal arms (Fig. 3, P). On attaining their definitive condition the reproductive bodies with the more numerous attachments are especially distinguished by irregularity of shape. Promiscuous variations in outward form are, however, by no means infrequent among mesially intercalary chlamydospores with 2 hyphal attachments.

In most cultures of *Conidiobolus inordinatus* the chlamydospores contain numerous globules about 1 μ wide (Fig. 3, B, a, b; D–V), although in many instances the protoplasm near the hyphal attachments is of homogeneous consistency. The resemblance in texture of cellular contents provides good reason to hold the species more closely related to *C. globuliferus* Drechsler (1956) than to any other congeneric form. Chlamydospores in some old cultures show a single large globule surrounded by a layer which, except for a small quantity of granular material, appears of homogeneous consistency (Fig. 3, C). As these chlamydospores reveal no marked thickening of the enveloping wall it seems unlikely that they have undergone conversion into zygospores or azygospores. Rather similar reorganization of contents has been observed at times in the globose and the elongated conidia of *C. heterosporus* Drechsler (1953). The strongly vacuolated condition of aging conidia of *C. denaeosporus* may denote similar though less pronounced modification.

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The history of a science is the science itself.—GOETHE.

MALACOLOGY.—*The subgenus* Halopsephus *Rehder, with notes on the Western Atlantic species of* Turbo *and the subfamily Bothropomatinae Thiele.*

ROBERT ROBERTSON, Museum of Comparative Zoölogy, Harvard University. (Communicated by Harald A. Rehder.)

(Received June 21, 1957)

Study of the Caribbean turbinid genus *Halopsephus* Rehder (1943) has led to the conclusion that the single species—*H. pulchra* Rehder—belongs in the genus *Turbo*, with *Halopsephus* ranked as a subgenus. This necessitates renaming the species, for there is a prior *Turbo pulcher*. A growth series was recently dredged off the eastern coast of Great Abaco in the northeastern Bahamas and this has made possible comparisons with other turbinids. Notes on the four Recent Western Atlantic species of *Turbo* now recognized are here included. The conclusion is also reached that the subfamily Bothropomatinae, based by Thiele (1924) on a single specimen from the Red Sea, is founded on a juvenile turbinid (possibly *Turbo*) and is therefore invalid.

I wish to thank Dr. Harald A. Rehder, United States National Museum, Washington, D. C. (U.S.N.M.), for much assistance, for having authorized study of the radula of the holotype of *Halopsephus pulchra* under his care, and for allowing me to rename the homonym resulting from the change in rank of *Halopsephus*. The species is here renamed *Turbo* (*Halopsephus*) *haraldi*, after Dr. Rehder. Help was also received from Dr. Myra Keen, Stanford University; Dr. K. Oyama, Tokyo; Dr. W. P. Woodring, U. S. Geological Survey, Washington, D. C., and Drs. W. J. Clench and R. D. Turner, Museum of Comparative Zoölogy, Harvard University (M.C.Z.). A juvenile specimen of *Turbo castanea* was examined at the Academy of Natural Sciences of Philadelphia (A.N.S.P.).

Family TURBINIDAE

Genus **Turbo** Linnaeus

Turbo Linnaeus, Syst. Nat., ed. 10: 761. 1758. Type species: *Turbo petholatus* Linnaeus, 1758 [Indo-Pacific], by subsequent selection, Montfort, Conch. Syst. **2:** 203. 1810.

Adult shell turbinate or trochoid, solid, nacreous within; aperture circular. Operculum calcareous, paucispiral. Five pairs of radular laterals; centrals varied (Troschel, 1878).

Subgenus **Turbo**, s.s.

Adult shell smooth, polished, imperforate; operculum smooth and polished at the center, granulose at the edges. Body of central tooth of radula expanded posteriorly into supporting wings; basal plate beneath this.

Turbo pittieri Dall (1912) from the Upper Pliocene (*fide* W. P. Woodring, *in litt.*) of Limón, Costa Rica, may belong in this subgenus.

Subgenus **Halopsephus** Rehder

Halopsephus Rehder, Proc. U. S. Nat. Mus. **93:** 191. 1943. Type species: *Halopsephus pulchra* Rehder, 1943 [= *Turbo* (*Halopsephus*) *haraldi* Robertson, 1957], by original designation.

Adult shell smooth, polished, imperforate; convex outer surface of operculum sculptured by one whorl of axial, retractively curved, rugose riblets. Radula (Fig. 3) similar to *Turbo*, s.s.

Monotypic.

Turbo (Halopsephus) haraldi, n. name

Figs. 1–3

Halopsephus pulcher Rehder, Proc. U. S. Nat. Mus. **93:** 191, pl. 20, figs. 3, 10. 1943; (corrected to *pulchra*) Poirier, An up-to-date systematic list of 3200 seashells from Greenland to Texas, p. 26 (mimeogr.). 1954; non *Turbo pulcher* Dillwyn, Catal. Shells **2:** 855. 1817; non *Turbo pulcher* Reeve, Conch. Systematica **2:** 167. 1842.

Description.—Adult shell solid, broadly conical, 11 mm high, nearly smooth, imperforate. Early nuclear whorls planate, white. Juvenile (3 whorls) carmine, with two carinae at the periphery, the upper one bearing short flattened spines; broadly umbilicate, the umbilicus bordered by nodes (Figs. 1–2). Lower carina enclosed in succeeding whorls; upper (stellate) carina becoming obscure in the third and fourth whorls. Umbilicus closed by parietal callus at this stage. Adult (5¼ whorls) cinnamon-rufous to apricot orange, spotted with white, palest at the base. Juvenile operculum with a subcentral pit (Fig. 1), mi-

nutely granulate. Adult operculum as in subgeneric description above.

Measurements.—As follows:

	Height	*Width*
Holotype	11.2 mm	11.0 mm
Paratype	6.0	6.0

Types.—Holotype, U.S.N.M. 500638. "Dredged off Lazaretto, Barbados, in shallow water on rocky bottom by John B. Henderson, Jr., while on the Smithsonian–University of Iowa 1918 Expedition." Paratype, U.S.N.M. 500639. "On the same trip off Payne's Bay Church, Barbados, in 50 fathoms on sandy and stony bottom" (Rehder, 1943).

Other specimens examined.—Six specimens (one alive) dredged in 37½ to 41½ fathoms about 3 miles ENE. of North Point, Elbow (Little Guana) Cay, off the eastern shore of Great Abaco, Bahamas, on August 5, 1955, by the writer (M.C.Z. 212954). One specimen (poor condition) dredged about 1 mile ENE. of the preceding station on the same day, in 50 fathoms (M.C.Z. 212955). All these Bahamian specimens are juvenile.

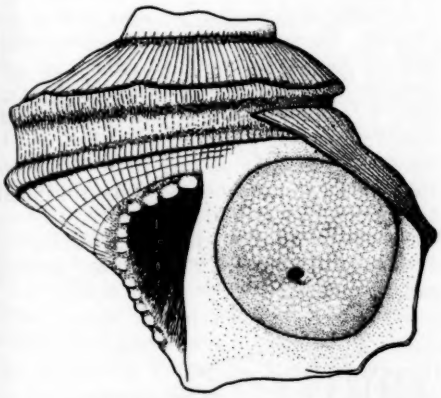

FIG. 1.—*Turbo* (*Halopsephus*) *haraldi* Robertson. Juvenile (2.1 mm in width), apertural view. Great Abaco, Bahamas (M.C.Z. 212954).

Range.—The known range of this species, previously known only from two specimens from Barbados, is now extended nearly 1,500 miles, to Great Abaco, northeastern Bahamas. Only nine specimens in museums are known to the writer at the present time. Undoubtedly more dredging in the Caribbean sublittoral will bring to light additional material at other localities.

Ecology.—The bottom on which the specimens were dredged near Great Abaco (37½ to 50 fathoms) is rocky, covered with calcareous algae, sponges, bryozoa and tunicates. Since most of these organisms are red the scarlet shell color may be protective. The one live juvenile was found in a red sponge.

Subgenus **Taeniaturbo** Woodring

Taeniaturbo Woodring, Mioc. Moll. Bowden, Jamaica **2** Carnegie Inst. Washington Publ. 385: 7, 408. 1928. Type species: *Turbo canaliculatus* Hermann, 1781, by original designation.
Taenioturbo 'Woodring' of Rehder and Abbott.

Spirally ribbed; initial whorls red; obsolete spiral sculpture on outer surface of operculum.

Turbo (Taeniaturbo) canaliculatus Hermann

TURBO (*canaliculatus*) Hermann, Der Naturforscher **16:** 52, pl. 2, figs. 1–2. 1781. No locality cited. Hedley & Pilsbry, Nautilus **26:** 46. 1912.
Turbo spenglerianus Gmelin, Syst. Nat., ed. 13: 3595. 1791. "Oceano indico" [sic].

This is not the *Turbo canaliculatus* of either Gmelin or Kiener.

Range.—Southern Florida, the Greater Antilles, Guadeloupe, possibly south to Bahia (Salvador), Brasil.

Turbo (Taeniaturbo) filosus (Wood)

Trochus filosus Wood, Suppl. Index Testac.: 17, pl. 5, *Trochus*, fig. 23. 1828. No locality cited.
Turbo cailletii Fischer and Bernardi, Journ. Conchyliologie **5:** 294, pl. 9, figs. 10, 11. 1857. "Côtes de la Basse-Terre (Guadeloupe). Recueilli sur la nasse d'un pêcheur."

Range.—Southern Florida, the Bahamas, Cuba, west to Yucatán and Nicaragua (?), and south to Guadeloupe.

Subgenus **Marmarostoma** Swainson

Marmarostoma Swainson, Zool. Illustr. (2) **1:** pt. 3, pl. 14. 1829. Type species: *Turbo chrysostomus* Linnaeus, 1758 [Indo-Pacific], by original designation.
Senectus 'Humphreys' Swainson, Treat. Malac.: 206, 213–215, 348. 1840. Type species: *Turbo chrysostomus*, by subsequent selection, Herrmannsen, Indic. Gen. Malac. **2:** 438. 1848.
Marmorostoma 'Swainson' of Gray and many subsequent authors.

Shell spiny or nodulose; operculum smooth, minutely granulated, or obliquely striate at the edge. Radula as in *Turbo*, s.s.

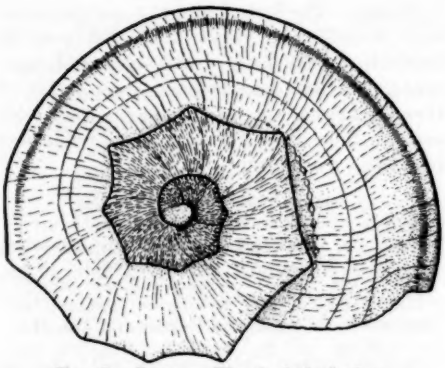

FIG. 2.—Same as Fig. 1. Apical view.

Turbo (Marmarostoma) castanea Gmelin

Turbo Castanea Gmelin, Syst. Nat., ed. 13: 3595. 1791. "*Habitat in* mari, Americam australem *alluente*."
Turbo crenulatus Gmelin, *ibid.* 1791. No locality cited.
Lunatica granulata Röding, Mus. Bolten.: 102. 1798; non *Turbo granulatus* Gmelin, 1791.
Turbo mammillatus Donovan, Nat. Hist. Brit. Shells **5:** pl. 173. 1804. "Scilly rocks, at the western extremity of Cornwall" (England) ballast.
Turbo hippocastanum Lamarck, Anim. sans Vert. **7:** 47. 1822. "Mers de l'Amérique australe."
Trochus (*Turbo*) *quadriseriatus* Anton, Verzeichniss Conch.: 59. 1839. No locality cited.
Turbo virens Philippi (ex Anton MS), Zeitschr. Malak. **5:** 99. 1848. No locality cited.

The specific name *castanea* was used by Gmelin as a noun in apposition.

Range.—Florida, the Bahamas, and the Greater Antilles, north (probably sporadically) to North Carolina, Bermuda (fossil); west to Campeche and Yucatán, and south through the Lesser Antilles to Trinidad and Margarita Island. *Turbo* (*Marmarostoma*) *squamiger* Reeve, 1843, is probably the Eastern Pacific analogue.

Lives on *Thalassia testudinum* in the Bahamas.

KEY TO THE RECENT WESTERN ATLANTIC SPECIES OF TURBO, S.L., BASED ON ADULT SHELLS

1. Spirally nodulose; initial whorls not red. ..... *castanea*
   Spirally ribbed or nearly smooth; initial whorls red 2
2. Nearly smooth, reddish orange, mottled with white; operculum strongly sculptured exteriorly with spiral riblets ..... *haraldi*
   Spirally ribbed, brown or greenish; obsolete spiral sculpture on outer surface of operculum 3
3. Imperforate; suture channeled; spiral ribs subequal; up to 93 mm high ..... *canaliculatus*
   Umbilicate; flat subsutural area; spiral ribs unequal; less than 30 mm high ..... *filosus*

DISCUSSION

The similarity of *Halopsephus* to *Turbo*, s.s., is striking; the main difference between the two is that the outer surface of the operculum of the latter is smooth, while in the former it is ribbed when adult. *Halopsephus* is smaller than *Turbo*, s.s. For these reasons *Halopsephus* is here reduced to the rank of a subgenus of *Turbo*.

When juvenile, *Turbo* (*Halopsephus*) *haraldi* is very similar in shell form to juvenile *Turbo* (*Marmarostoma*) *castanea*. Pilsbry and McGinty (1945) have illustrated the latter from a shell dredged in 50 fathoms off Palm Beach, Fla., which I have examined (A.N.S.P. 181123). This specimen was obtained dead, so the juvenile operculum is not yet known. The chief difference between juveniles of the two species is that *T. haraldi* is bright carmine, while *T. castanea* is whitish.

Juvenile *Halopsephus* is also similar to juvenile *Taeniaturbo*. *Turbo canaliculatus* and *T. filosus* are both carmine and are initially stellate at the periphery, but differ from *T. haraldi* in the early development of numerous strong spiral ribs, one of which arises from the spinose carina. In *T. haraldi* the carina becomes obscure in the third and fourth whorls. The juvenile of a Miocene species from Bowden, Jamaica, referred by Woodring (1928) to *Taeniaturbo*, is also similar to *T. haraldi*.

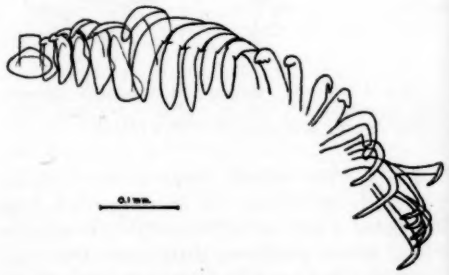

FIG. 3.—*Turbo* (*Halopsephus*) *haraldi* Robertson [= *Halopsephus pulchra* Rehder]. Radula of holotype (U.S.N.M. 500638). Barbados.

An opercular pit like that in juvenile *Halopsephus* is frequent among young (and some adult) turbinids. It can be seen in several other species of *Turbo* and also in the Caribbean *Astraea* (*Lithopoma*) *caelata* (Gmelin), among others.

Not all species of *Turbo* have a nodulate ridge bordering the juvenile umbilicus. One that does not is *Turbo stamineus* Martyn [= *Turbo* (*Ninella*) *torquatus* Gmelin, 1791], illustrated by Kesteven (1901). The umbilicus persists in the adult in this Australasian species.

Thiele (1924) has founded a subfamily of the Turbinidae—the Bothropomatinae—on a single specimen from Kosseir (Quseir), Egypt, near the northern end of the Red Sea. This he named *Bothropoma isseli*. The characters of the shell suggest that it is juvenile. There are strong spiral ridges, the umbilicus is bordered by a nodulate ridge and the operculum has a large central pit. There are four pairs of radular laterals (Thiele, 1924, 1929). This is probably a young *Turbo*, despite the fact that all species of *Turbo* and the related genus *Astraea* that have so far been studied have five pairs of radular laterals. Thiele's specimen may have been abnormal (whole longitudinal rows of radular teeth are sometimes absent teratologically among gastropods), or perhaps the radula as well as the shell of *Bothropoma* shows juvenile characters. The cusps of the *Halopsephus* radula are much more strongly serrate in the juvenile than in the adult, but there are five pairs of laterals in the juvenile. The cusps in *Bothropoma* are strongly serrate. The central tooth, as figured by Thiele (1924), has posterior supporting wings, similar to those in *Turbo*, s.s., *Halopsephus*, and *Marmarostoma*. Thiele (1935) has subsequently reported *Bothropoma* from Western Australia as well as the Red Sea.

The Japanese turbinid *Liotia pilula* Dunker, 1860, designated the type species of a new genus—*Neocollonia*—by Kuroda & Habe (1952, 1954), was placed by them in the Bothropomatinae on the basis of what is here considered insufficient evidence of close affinity with *Bothropoma:* merely that the shell is spirally ribbed, has an umbilicus bordered by a nodulate ridge, and that the operculum has a central pit. The radula is very simple; the cusps are not serrate as in *Bothropoma*, and there are five rather than four pairs of laterals. This species has since been incorrectly transferred to the genus *Bothropoma* by Kuroda (1956, spelled *Bathropoma*).

An umbilicus bordered by a nodulate ridge is here regarded as a primitive character among turbinids, for the following reasons. In early ontogenetic stages most turbinids show these features, and the operculum usually has a central pit on the outer surface. Furthermore, perforate shells must necessarily have originally preceded imperforate shells in the phylogenies of asymmetrically coiled aspidobranchs (archaeogastropods), for these were undoubtedly derived from bellerophonts, which were symmetrically coiled (isostrophic). *Neocollonia* is here regarded as a primitive (or possibly neotenous) turbinid, as it shows these primitive characters when adult and has a very simple radula.

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"TERRIBLE LIZARDS"

Dinosaurs were the dominant animals on earth for approximately 130 million years. Man and his more or less humanlike forerunners have been here, at the most, less than 2 million years, and all human history covers a maximum of little more than 10,000 years. The earliest mammallike creatures date back hardly more than 150 million years.

The story of this long supremacy of a race of extinct reptiles, which first appeared 200 million years ago and persisted to the dawn of the age of mammals about 70 million years ago, is told by Dr. David H. Dunkle, of the Smithsonian Institution's Division of Vertebrate Paleontology, in a 24-page illustrated booklet recently published by the Institution.

These reptiles, whose nearest extant relatives are the vastly different birds and crocodiles, included the largest creatures ever to inhabit the land. Some of them, however, were no bigger than chickens. During their long tenure of existence they underwent fantastic variations. Many walked upright on their hind legs. Some got about on all four legs. Some developed heavy suits of bony armor.

Most illustrations of restorations of these great reptiles render them as rather awesome creatures. Actually, Dr. Dunkle says, the majority were plant eaters and probably rather peaceful. Some, however, became flesh eaters and must have been terrifying.

The new booklet's descriptions of the "terrible lizards" are based partly on the fossil material in the U. S. National Museum collection, one of the best in the world. The reptiles are divided into two major groups, distinguished by the structure of the pelvic bones. That of one is lizardlike, of the other birdlike. First were the so-called Saurischia, which included all the flesh-eating types and a few of the plant eaters. The birdlike group appears somewhat later. They were the Ornithischia, all of them plant eaters. Among these the bone armor-plate was developed. Apparently it was needed for protection against the flesh-eaters. Those without such natural devices either escaped from their enemies by speed and agility or found protection in tremendous size and weight. Many of these were amphibious, retreating to river and swamp environments.

All the dinosaurs, Dr. Dunkle points out, presumably were stupid animals. This certainly is true if brain size is directly related to intelligence. The bony capsule enclosing the brain occupied a very small portion of the skull. It has been postulated that the dinosaurs' diminutive brains may have been a major cause of their extinction when they came into competition with the more alert primitive mammals.

"But," says Dr. Dunkle, "the complete disappearance and extinction have never been entirely explained. However, throughout earth's history, great changes in its surface have taken place, caused by the upheaval of mountains and the enlargement of continents and by the destructive tearing down of these by the myriad factors of erosion. Life must adapt itself to the consequent variations in climate, food supply, and other environmental conditions. When it cannot, that life vanishes. Such, scientists suppose, was the fate of the dinosaurs."

Lack of brains, therefore, may have been a relatively minor factor, considered over many millenniums.

The ultimate origin of the dinosaurs is a moot question, but, Dr. Dunkle points out, there was a group of reptiles fairly abundant in the Triassic period of geological history about 200 million years ago. These were the thecodonts. They were not themselves dinosaurs but had some of the same skeletal characteristics of the earliest of these reptiles.

Copies of Dr. Dunkle's booklet, entitled "The World of the Dinosaurs," may be purchased for 50 cents from the Smithsonian Institution, Washington 25, D. C.

I have been very careful to write nothing but what was the product of faithful observation, and neither suffered myself to be deceived by idle speculation, nor deceived others by obtruding anything upon them but downright matter of fact—

THOMAS SYDENHAM (*1624—1689*)